AQUEOUS THERMOLYSIS OF MONOSUBSTITUTED BENZENES WITH A TWO-CARBON ATOM SIDE CHAIN AND OF NITROGEN HETEROCYCLES

By

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LIAISON WITH OTHER LABORATORIES

The research program on aquathermolysis at the University of Florida has been carried out in close collaboration with the EXXON Corporate Research Laboratories at Clinton, New Jersey, with liaison also with their laboratory at Baytown, Texas. However, all the work presented in this dissertation has been carried out by the author with the sole exception of chapter 2, which describes the results of a joint project in which Andrzej Lapucha, Franz Luxem and Ramiah Murugan at the University of Florida collaborated with Giuseppe Musumarra of the University of Catania, Italy.

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Major Department: Chemistry

The thermal reactions of organic functional groups were systematically investigated under various conditions. Two different compound classes were studied: i) monosubstituted benzenes with a saturated two-carbon atom side chain, or oxygenated at the α-, ß-, or α- and ß-positions, and ii) the heterocycles pyrrole, 2,5-dimethylpyrrole, indole, 2-methylindole, 3-methylindole and 2,3-dimethylindole. The reaction conditions were 150-350°C in i) cyclohexane, ii) water and iii) water with acid or base as additives.

Acetophonone and ethylbenzene were the least reactive compounds of the substituted benzene series. Ethylbenzene underwent mainly radical reactions. Even with acid catalysis and a reaction time of 21 days, only a 2% conversion was

obtained. Acetophenone gave triphenylbenzene as major product. Styrene completely polymerized in water at 250°C, but formed dimers, trimers and tetramers in cyclohexane under the same conditions. The major reaction pathways of 2-phenylethanol, α-phenylethanol and phenylethane-1,2-diol in water were disproportionation, whereas thermal dehydration predominated in cyclohexane. Phenylacetaldehyde and phenylglyoxal very readily underwent aldol condensation and disproportionation reactions under aqueous conditions. Thermal conditions led to a significantly higher amount of polymeric products. Phenylacetic acid showed little reactivity in water, but formed dibenzylketone in cyclohexane at 250°C. Benzoylformic acid and mandelic acid were highly reactive and showed mainly decarboxylation, decarbonylation and disproportionation under both thermal and aqueous conditions.

All heterocycles tested did not show any significant conversion under thermal conditions. At 350°C in water and 250°C in acid, alkyl transfer reactions were observed. Heteroatom removal was found in the case of 2,5-dimethylpyrrole in water, whereas cycloadditions took place with acid catalysis. Heteroatom removal was more difficult in the case of the indoles, but at 350°C in 10% phosphoric acid, significant amounts of aniline, methylanilines, o-cresol and phenol were found.

CHAPTER 1
IMPORTANCE OF AQUEOUS THERMOLYSIS

1.1 Introduction

The reactions of organic molecules with water have not been thoroughly investigated. Only very little is known about the chemical reactions of organics in an aqueous environment, particularly at temperatures from 150°C to just below the critical point of water (375°C). Ample examples can be found in the literature on the behavior of organic compounds in water at much higher temperatures (≤400°C). However, at these temperatures, simple thermolysis (cracking) may become a significant side reaction at the cost of aquathermolysis. Water recently attracted attention in the coal liquification processes [87CT636, 86CN31], in the hydropyrolysis of coal with steam [86FU1571], in the recovery of heavy oil [86FU4, 84AJR15] and in the depolymerization of kerogen [84OG267].

Much research in this area is devoted to the extraction of coal with supercritical water [88FC292]. Under those conditions, temperatures range between 374 - 400°C and pressures of approximately 400 Pa are used. Efforts are made to optimize the role of steam (water) in coal pyrolysis [86FU1571] or in the removal of heteroatoms such as nitrogen and sulfur, which are present in fossil resources [86FU827], in the upgrading process of coal, shale oil, etc. Despite the obvious interest, very little attention has been paid to the chemical reactions that might be occurring in an aqueous environment at temperatures of 200 - 350°C (i.e. ~200 - 250°C is a typical temperature range in the steam recovery of heavy oils [84AJR15, 86FU4]).

It is the aim of the present work to fill this void in the literature, to provide the scientific basis to better understand the effect of water at high temperatures and pressures

on organic compounds and, at the same time, to investigate the possibility of denitrogenation of heterocycles in such systems. To achieve this objective, monosubstituted benzenes and heterocyclic compounds were chosen as models which are believed to be representative of structures found in coal or oil shales [84FU1187].

Chapter 3 focuses on monosubstituted benzenes with a two-carbon atom side chain which is oxygenated at the α-, ß-, or the α- and ß-positions, as well as the pure hydrocarbon analogs. Pyrroles and indoles represent the heterocyclic compounds and are discussed in Chapter 4. All reactions were carried out both in water alone and in water with acid or base as an additive. In order to differentiate between thermal and aqueous reactivity, each compound was also tested using cyclohexane as solvent, based on the assumption that cyclohexane would be inert under the reaction conditions.

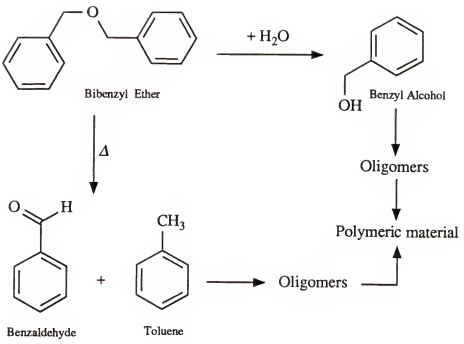
Chapter 2 is devoted to the prediction of gas chromatographic respose factors. For the quantitative evaluation of the reaction mixtures, it was necessary to find a reliable method to determine response factors (RF) for flame ionization detectors (FID). This method was developed jointly between our group and other researchers [89TCMip], and is based on the soft independent modeling of class analogy (SIMCA) method for the statistical evaluation of data.

1.2 Background

Water was selected as a solvent, not only because nature itself provides an excellent example (fossil resources and numerous clay minerals formed in an aqueous environment), but also because of its unique properties. Some of these properties include i) the temperature and pressure dependence of the dielectric constant, ii) the amphoteric character of water, and iii) its solubility profile towards non-polar organic materials at high temperatures and pressures [70PAC13, 85AG(E)1026].

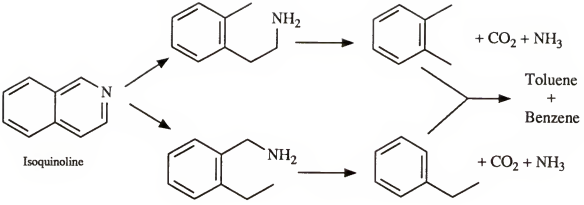
Many of the early studies on the participation of water in the transformation of organic compounds were conducted with clay as a catalyst. Clay is believed to play a role in the formation of hydrocarbons in petroleum [74MI1]. For example, the dimerization of fatty acids was carried out at 200 - 260°C with a steam pressure of 5 - 10 Pa. The presence of clay in amounts as low as 1% and the use of methyl and ethyl esters decreased the unwanted polymer by-product. The yield was up to 60% of dimer in the case of oleic acid [35USP1, 57USP1]. Comparative studies on fatty acids (which are thought to be among the precursors of crude oil) under anhydrous and aqueous conditions showed a significant difference between aqueous and thermal reactivity. Behenic acid ($n\text{-}C_{21}H_{43}COOH$) was reacted with betonite clay in sealed tubes for 89 and 760 hours at 200°C [64SE1451]. It was found that behenic acid degraded into hydrocarbons with chain lengths from C_3 to C_5, but higher molecular weight paraffins (chain extension) were also found (C_{14} - C_{34}) with the decarboxylation product $C_{21}H_{44}$ of behenic acid as the major product. The total amount of hydrocarbons increased with the heating time, whereas the amount of unsaturated hydrocarbons decreased. The ratio of unbranched to branched paraffins changed significantly in the presence of water and was greater in water than under anhydrous conditions (4 vs. 0.1). The higher amount of branched hydrocarbons may suggest Wagner-Meerwein rearrangements as a major reaction pathway.

The reactions of dibenzyl ether were investigated in water at 374, 401 and 412°C and compared to simple pyrolysis at the same temperatures [85FU635]. The major reaction products in water were benzyl alcohol, toluene, benzaldehyde and oligomers. In comparison, the neat pyrolysis was much slower and did not give benzyl alcohol as a product, which is evidence for a direct participation of water in the process (scheme 1.2.1).

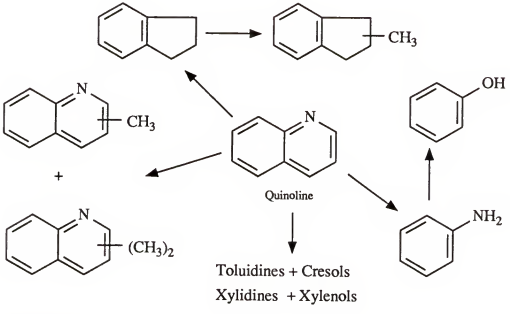


Scheme 1.2.1

Supercritical water (400 - 500°C) was used to probe if water could be of assistance in removing nitrogen from heterocyclic compounds [86FU827]. Isoquinoline and quinoline were chosen as model compounds. At 400°C for 48 hours with no water added, 90% of isoquinoline was recovered with no measurable volatile products or char present. In the presence of water, approximately 50% conversion took place, of which 30 - 55 mole% consisted of aromatics (aniline, phenol, xylene, ethylbenzene, etc.) and about two thirds of the nitrogen was fixed as ammonia. Addition of $ZnCl_2$ increased the extent of the reaction, but had no impact on the product distribution. The reactions of isoquinoline and quinoline in water are summarized in schemes 1.2.2 and 1.2.3.



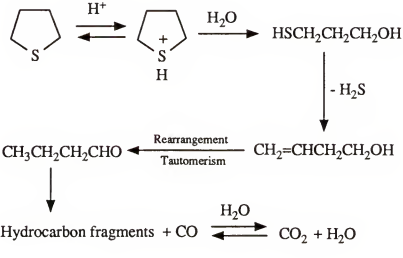
Scheme 1.2.2



Scheme 1.2.3

Very interesting results have recently been obtained by Peter D. Clark and coworkers, who carried out the hydrolysis and thermolysis of thiophene and tetrahydrothiophene under various conditions [83FU959]. The reactions were performed in a sealed quartz tube to avoid catalytic effects caused by the metal wall of an

autoclave. The temperature was 300°C and pressures ranged from 3.35 MPa to 8.6 MPa. In both hydrolysis and thermolysis, a great variety of products was formed. In the presence of water, carbon dioxide was formed, which was evidence that hydrolyisis occurred, since water was the only oxygen source. Among a great range of gaseous products like CO_2, H_2S and alkanes of chain lengths between C_1 and C_5, various liquid products were also obtained, of which butanethiol was predominant. Alkyl sulfides, disulphides and alkyltetrahydrothiophenes were also products. Without water, a significantly greater amount of small molecules was obtained. A suggestion for the pathway of the hydrolysis of tetrahydrothiophene is given below (scheme 1.2.4).

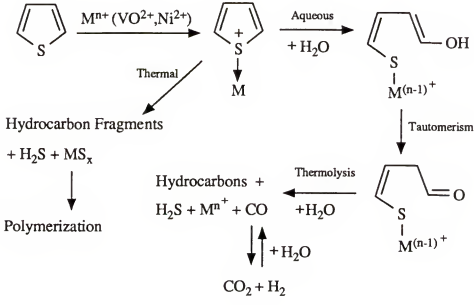


Scheme 1.2.4

In the presence of acid, the hydrolysis of tetrahydrothiophene was about 35 times faster, and that of thiophene 30 times faster, than without acid. For both, the hydrolysis at low pH values resulted in more polymeric product. At higher pH values (above 7) only tetrahydrothiophene showed any marked reactivity [84FU125].

Vanadyl sulfate, $VOSO_4$, interacted strongly with thiophene. It was found that the system of aqueous vanadyl sulfate and thiophene was as reactive as tetrahydrothiophene with water. Comparatively, the reaction of tetrahydrothiophene and water was 8 times faster than that of thiophene with water. The major gaseous product in the reaction of thiophene and vanadyl sulfate with water was H_2S, which is believed to be a result of a coordination of the metal to the sulfur atom of thiophene. Some amount of the formed hydrogen sulfide reacted with the vanadyl sulfate to sulfides VX_x with various stoichiometry. Carbon dioxide was a minor product in this reaction and it is therefore believed that the preferred pathway for this reaction is thermolysis of the formed metal complex as shown in scheme 1.2.5 [84FU1649].

The nickel system also showed some catalytic effects, but far less than vanadyl sulfate. In the experiments with nickel salts, CO_2 was the major product and H_2S was consumed by the aqueous nickel species [84FU1649].



Scheme 1.2.5

CHAPTER 2
PREDICTION OF GAS CHROMOTOGRAPHIC RESPONSE FACTORS BY THE PLS METHOD

2.1 Introduction

The advent of gas chromotography/mass spectrometry (GC/MS) has dramatically improved the capability to reliably identify and quantitatively analyze complex mixtures, which just two decades ago would have been impossible to accomplish. The advantages of GC/MS are particularly evident in those cases in which many compounds are formed, as the method allows the identification of the products as well as the determination of their proportions. However, for the quantitative estimation of concentrations, it is nececessary to know the response factor (RF) for each compound under the experimental conditions used (detector, temperature, carrier gas, flux, etc.). The experimental determination of the RF is routine, but requires the availability of a pure specimen of each compound, the preparation of solutions at given concentrations, and the gas chromotographic analyses. In the case of mixtures containing many products, this experimental procedure is at best time consuming, but can also be quite impractical because of the inavailability of samples of many of the products. Because of the complex product mixtures (up to 40 different compounds) encountered in the present work on aqueous [89EF1ip] thermolysis, the estimation of unknown response factors was necessary so that reaction products could be analyzed quantitatively by the GC/MS technique. There was no readily available and generally applicable published procedure that allowed to do this. It was therefore necessary to develop a procedure which would routinely allow a reliable estimation of response factors from molecular structures [89TCM].

2.2 Response Factor-Structure Relationship

The Flame Ionisation Detector (FID) is the most widely used GC detector, having achieved great popularity in the early 1960s [64JGC173, 68JCG135, 68JCG497]. Rugged FIDs which are relatively stable with regard to small changes in operational parameters and with good sensitivity and linearity are now available. The FID shows similar response factors for all hydrocarbons [67JGC68] and also responds to other analytes while remaining unresponsive to permanent gases or carrier gas impurities and water.

There are three basic methods for processing data for quantitative analysis, the Normalization Method, the External Standard Method and the Internal Standard Method [87MI1]. The Normalization Method is rarely employed because it requires that the dectector gives the same response to all solutes. The Internal Standard Method gives the most precise and accurate results but requires the selection of a standard that is resolved from all the sample constituents. Furthermore, the solutes of interest cannot, themselves, be selected as standards. The External Standard Method is a little less precise and accurate than the Internal Standard Method, but allows the solutes of interest themselves to be used as standards and makes no extra demands on the chromatographic resolution. However, different compounds have different detector responses; therefore, it is necessary to determine correction factors or the so-called Response Factors (RF).

Two important features of the FID are generally accepted. For hydrocarbons, the FID response is proportional to the carbon number of the hydrocarbons, often called the "equal-per-carbon response," and the FID response of substituted hydrocarbons is always less than that of the parent hydrocarbon. The concept of the effective carbon number (ECN) was introduced many years ago [62MI1-3] and has also been proposed for the

calculation of response factors for compounds which cannot be obtained in pure form [85JCH333]. An important factor which must be considered in the study of FID response factors is the performance of the GC instrument. In most earlier studies, packed columns and vaporization injection techniques were used. Accuracy and precision of peak areas were limited by the resolution offered by packed columns. Bleeding of the stationary phase of the column commonly led to broadening and tailing of peaks and poor base lines. Discrimination against both low and high boiling point compounds occurs in the vaporization injection technique. These occurrences adversely affect the accurate evaluation of FID response factors for many compounds.

During the last few years, the development of WCOT (Wall Coated Open Tubular) GC (also called high-resolution GC) has resulted in improved quality GC analysis [84AC2124]. Also, the introduction of cold on-column injection has minimized, or completely eliminated, the discrimination against both low and high boiling point compounds during sample injection [81JCHR85].

The RF value of a compound differs from instrument to instrument. Therefore, in the practical use of RF for quantitative analysis, the responses of standard compounds and samples must be determined on the same instrument and under the same operation conditions.

However, W. A. Dietz first reported tabular GC responses for FID in 1967 [67JGC68]. He gave no experimental details, but the correction factors were probably calculated using equation (1), later used by McNair and Bonelli [69MI1].

$$RF = \frac{\text{Weight of Standard x Area of Compound}}{\text{Weight of Compound x Area of Standard}} \quad \cdots\cdots (1)$$

The values so obtained are called "divisor RF"; the area of each peak is divided by the relative sensitivity (RF), and then normalized to obtain weight percent. The standard most commonly used was n-heptane with RF = 1. Recently (1985), J. T.

Scanlon and D. E. Willis [85JCH333] summarized previous work and proposed the use of the ECN (effective carbon number) concept for the calculation of response factors for compounds not available in pure form and defined the RF as the inverse of equation (1) (equation 2).

$$RF = \frac{\text{Weight of Compound x Area of Standard}}{\text{Weight of Standard x Area of Compound}} \quad \cdots\cdots (2)$$

This equation is based on a response factor of 1.0 for the standard (n-heptane) and the RF so obtained is called "multiplier response factor," i.e., each peak area has to be multiplied by the realtive sensitivity (RF) and then normalized to obtain the weight percent. The relative weight response factor can be transformed to the relative molar response factor (equation 3).

$$RF_{mol} = RF \times \frac{\text{MW of Standard}}{\text{MW of Compound}} \quad \cdots\cdots (3)$$

The ECN is then calculated by equation (4) or equation (5).

$$ECN_{comp.} = \frac{\text{ECN Standard}}{RF_{mol}\ \text{Compound}} \quad \cdots\cdots (4)$$

$$ECN_{comp.} = \frac{\text{MW Compound x ECN Standard}}{\text{MW Standard x RF}} \quad \cdots\cdots (5)$$

Relative response factors from compounds whose ECN is known or can be calculated from the contributions of the various groups in the molecule are easy to obtain from equation (6).

$$RF = \frac{\text{MW Compound x ECN Standard}}{\text{MW Standard x ECN Compound}} \quad \text{.....} \quad (6)$$

The use of ECN for the calculation of response factors for compounds which cannot be obtained in pure form [85JHC333] requires a knowledge of the dependence of the ECN on various heteroatoms and on functional groups in the molecule. Unfortunately, this relationship has not been extensively studied, and even for those classes of compounds for which the ECN can be calculated, discrepancies between calculated and measured RF commonly range to 25%, and for a few outliers (acids, diols) to as much as 75%.

2.3 Statistical Prediction of RF

As an alternative to the use of "hard" mathematical models based on theoretical equations, a new discipline, chemometrics, has recently developed parallel to the improvement of computing facilities. By means of chemometrics, the application of mathematical and statistical methods to chemistry [72JA5632], it is possible to design appropriate experiments and to extract information from available data using "soft" empirical mathematical models of local validity which explain the data within a given domain [81ACS(B)537]. In particular, Wold and coworkers have developed the method called SIMCA (Soft Independent Modelling of Class Analogy) based on disjoint principle components modelling by means of principle components (PCA) and partial least squares (PLS) [77MI1, 84MI1]. Application of the SIMCA approach to complex chromatographic data sets [87MI2] has already proved to possess great potential for i) the evaluation and selection of TLC eluent systems [84JCHR31] and ii) the identification

of drugs by PCA of standardized TLC data in four eluent mixtures [84JCH151], together with one gas chromatographic retention index on SE 30 [87JAT154].

A data set suitable for a multivariate analysis consists of a table (matrix) where a number (N) of experimental values (variables) is collected for each of the N chemical compounds (objects). Multivariate methods search for the structure of the data, i.e., they are aimed at recognizing systematic patterns, if present [72JA5632].

The PLS analysis is aimed at finding the relationship existing between one or more "dependent" variables and a group of explanatory variables. When there is more than a single dependent variable, we have two blocks of variables, and it is possible to define a "dependent" matrix $\underline{Y}$ and an "independent" matrix $\underline{X}$ [86ACA149]. The question under investigation is whether or not the members of the $\underline{Y}$ matrix can be described as a function of the members of the $\underline{X}$ matrix. Rather than computing principle components models for each of the two matrices and looking for a linear relationship between the principle components of these two blocks by a two-step procedure, the PLS algorithm achieves these two steps simultaneously.

The data matrix chosen for the reference set for the RF prediction contains 1800 elements for 100 objects (compounds) described by the 18 variables listed in table 3.2.1. Variable 1 (which is taken as the dependent variable in the PLS analysis) is the RF_{Dietz}. The explanatory variables (descriptors) selected are the molecular weight and the following series of descriptors of the chemical structure: the number of the C, H, O, N and S atoms; the numbers of multiple bonds C=C, C=O, C=N, C≡N; the number of rings; and the numbers of the $-CO_2H$, -OH (or -SH), -CHO, $C-CO_2-C$, $-NH_2$ and C-O-C (or C-S-C) functional groups. In the PLS analysis, the Dietz response factor is chosen as dependent variable and described as a function of 17 explanatory variables (variables 2-18). A three-component PLS model explains 84% of the variance in the RF_{Dietz} data. As a result of the foregoing treatment, RF values (y_{ia}) can now be predicted from the

PLS model parameter relationship which, in the present case, takes the form of equation below (equation 7).

$$RF = 0.991 - 0.000908\ x_2 + 0.00234\ x_3 + 0.00276\ x_4 - 0.112\ x_5 - 0.0711\ x_6 - 0.160\ x_7 + 0.00337\ x_8 - 0.0434\ x_9 - 0.476\ x_{10}\ 0.0777\ x_{11} + 0.00481\ x_{12} - 0.323\ x_{13} - 0.0536\ x_{14} - 0.206\ x_{15} - 0\ .0459\ x_{16} - 0.166\ x_{17} - 0.0675\ x_{18}$$

By inserting the appropriate x value for each descriptor, response factors can easily be calculated using equation (7) for any compound containing this range of functional groups. Figure 2.3.1 shows satisfactory Dietz RF predictions for most compounds in the reference set (circles). The RF average deviation of all 100 compounds in the reference set is 0.05 with an average percent deviation of 9.0%; for the test set (triangles), the average deviation is 0.09 (14.9%).

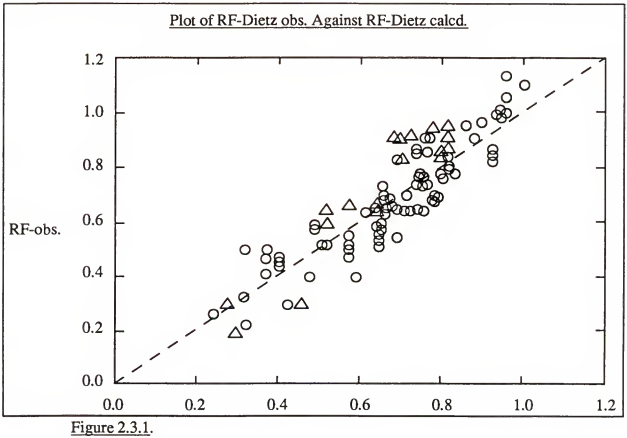


Figure 2.3.1.

Table 2.3.1. Explanatory Variables for Response Factor Calculation

Variables 2-18 are the "explanatory" variables (X Block);
variable 1 is the dependent variable

No.	Symbol	Variable	Weights[a]	Averages[b]
1	RF_{Dietz}	Response Factor	5.6106	3.9179
2	MW	Molecular Weight	0.0244	3.3323
3	C	No. of C Atoms	0.3167	2.1715
4	H	No. of H Atoms	0.1510	1.5040
5	O	No. of O Atoms	1.4428	0.8945
6	N	No. of N Atoms	1.2766	0.8298
7	S	No. of S Atoms	4.1897	0.2514
8	C=C	No. of C=C Double Bonds	0.6605	2.0014
9	C=0	No. of C=O Double Bonds	2.8075	0.3369
10	C=N	No. of C=N Double Bonds	1.6467	0.7081
11	C≡N	No. of C≡N Triple Bonds	3.6676	0.2934
12	Rings	No. of Rings	1.8165	2.1800
13	CO_2H	No. of Carboxyl Groups	4.1897	0.2514
14	OH or -SH	No. of Hydroxyl Groups	2.4875	0.4975
15	CHO	No. of Aldehyde Groups	4.1897	0.2514
16	$C\text{-}CO_2\text{-}C$	No. of Ester Groups	4.0775	0.2031
17	NH_2	No. of Amino Groups	2.8675	0.4015
18	C-O-C or C-S-C	No. of Ether or Sulfide Groups	3.0619	0.3674

[a] Factor required to autoscale the variables to unitary variance.

[b] Arithmetic means of the variables.

CHAPTER 3
AQUEOUS THERMOLYSIS OF MONOSUBSTITUTED BENZENES WITH A TWO-CARBON ATOM SIDE CHAIN

3.1 Introduction

Chapter three will focus on the aqueous thermolysis of monosubstituted benzenes with a two-carbon atom side chain, including saturated, unsaturated and oxygenated derivatives. Section 3.2 deals with ß-oxygenated side chains [89EF2ip]. The representative molecules are ß-phenylethanol, phenylacetaldehyde and phenylacetic acid. Hydrocarbon compounds, ethylbenzene, styrene, and acetylene are discussed in section 3.3 together with the α-oxygenated model compounds α-phenylethanol and acetophenone [89EF3ip]. Section 3.4 focuses on compounds oxygenated at both the α- and ß-positions, considering specifically phenylethylene glycol, mandelic acid, benzoylformic acid and phenylglyoxal [89EF4ip]. The following guidelines were adopted throughout chapter 3: for each section, Table 1 lists all the compounds encountered in the present work, either as reactants or as products. Table 2 records properties of authentic compounds used as starting materials or in the identification of products. Table 3 compares the mass spectral fragmentation patterns of the products with literature data used in their identification. Table 4 is devoted to compounds of which the structures were deduced from their MS fragmentation patterns, in the absence of suitable literature data for comparison. Each compound number in sections 3.2 through 3.4 refers only to chapter 3.

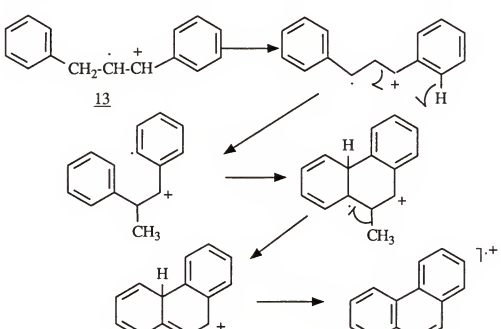
3.2 Oxygenated at the Side Chain ß-Position

3.2.1 Assignments of Structures

The structures of products **(9), (13-15), (17)** and **(18)** were deduced from and are supported by their mass spectral fragmentation pattern (Table 3.2.4).

Phenethyl acetate **(9)** shows the mass spectral behavior characteristic of esters of this type [67MI1(a)]: a weak molecular ion peak at m/e 164 and the typical α-cleavage for esters which produces the base peak m/e 43 CH_3CO^+. The fragment $PhCH{=}CH_2$ at m/e 104 results from an equally typical ß-elimination. The expected signal for ($C_7H_7^+$ tropylium) at m/e 91 (28% r.i.) is also present.

1,3-Diphenylpropene **(13)** displays the molecular ion as the base peak at m/e 194.



Scheme 3.2.1

The fragment at m/e 179 has been shown, in a publication which does not give the full structural details [66JCS(C)1955], to result from a rearrangement to a phenanthrene radical cation via expulsion of a methyl radical. Compound (**13**) also shows fragment ions at m/e 91 for ($C_7H_7^+$ tropylium) and at m/e 115 (benzocyclopentadienylium, $C_6H_4C_3H_3^+$).

2,3-Diphenylprop-2-en-1-al (**14**) gives the molecular ion at m/e 208 as the base peak and the strong M-1 peak typical for aldehydes [67MI1(b)] at m/e 207. The fragment ion at m/e 179 (loss of CHO) also supports the aldehyde structure (**14**). Cleavage of CH_2O gives $PhC{\equiv}CPh^+$ m/e 178.

Bis-(ß-phenylethyl) ether (**15**) shows the molecular ion peak at m/e 226. The base peak $PhCH_2CH_2^+$ at m/e 105 is formed via C-O bond scission [67MI1(c)]. Other characteristic fragment ions include ($C_7H_7^+$ tropylium) m/e 91 and Ph^+ m/e 77. This symmetrical ether (**15**) thus exhibits a fragmentation pattern similar to that of ß-phenylethyl methyl ether; neither can undergo a McLafferty rearrangement [67MI1(c)].

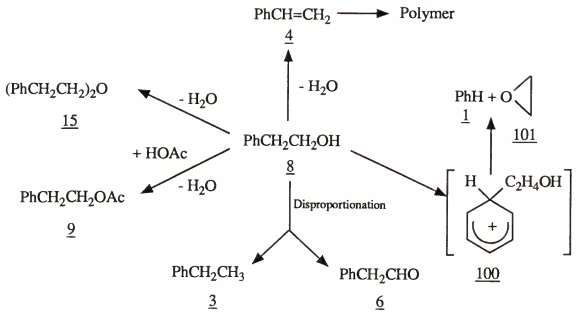
2,4-Diphenylbut-2-en-1-al (**17**) displays its molecular ion as the base peak at m/e 222 and the strong M-1 peak characteristic [67MI1(d)] for aldehydes at m/e 221. The loss of H_2O (possibly by cyclization to 2-phenylnaphthalene $C_{16}H_{12}$) gives a peak at m/e 204, and the usual loss [67MI1(d)] of CHO^+ results in m/e 193. The expected ($C_7H_7^+$ tropylium) m/e 91 is also present.

1,2,4-Triphenylbut-1-en-3-one (**18**) shows a molecular ion peak at m/e 298. The formation of m/e 91 ($C_7H_7^+$ tropylium) provides the base peak, whereas loss of $PhCH_2{\cdot}$ gives the fragment ion m/e 207. The fragment ion m/e 193 results from loss of $PhCO{\cdot}$.

3.2.2 Discussion of Results

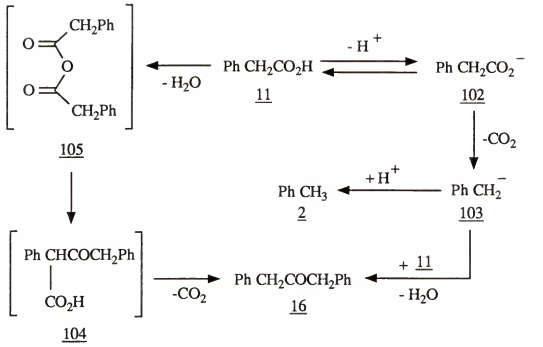
The overall product slate and proposed reaction pathways are shown in scheme 3.2.6 (with the exception of certain products formed in cyclohexane by the intervention of the solvent). Schemes 3.2.2 - 3.2.5 deal with proposed reaction mechansims which are discussed under the individual starting materials.

2-Phenylethanol **(8)** (Table 3.2.5). In cyclohexane the major reactions are the dehydrations to form either styrene **(4)** [42JCS(J)358], or the ether $PhCH_2CH_2OCH_2CH_2Ph$ **(15)**. There is a smaller amount of ethylbenzene **(3)** and phenylacetaldehyde **(6)** formed via disproportionation of **(8)**. Some toluene is found, which is probably formed via decarbonylation of phenylacetaldehyde **(6)** or decarboxylation of phenylacetic acid **(11)**. Earlier studies, however, have shown that nickel catalyzes the formation of small amounts of toluene and other compounds [40ADC(11)318]. Higher temperatures of up to 425°C result in a complete thermal breakdown of the molecule into H_2, CH_4, $PhCH_3$, CH_3OH, CO_2, CO, and water [28JA3067]. In water alone, reaction is much slower and the major process is again dehydration but now much more styrene **(4)** than the ether **(15)** is produced. The rate of reaction in water is accelerated by pyridine, and especially by acetic acid. The products from pyridine catalysis are mainly styrene **(4)** and some ether **(15)**, together with high boiling materials presumably formed by polymerisation of styrene **(4)** and phenylacetaldehyde **(6)**. Acetic acid gives mainly 2-phenylethyl acetate **(9)** but also appreciable amounts of benzene **(1)** and ethylbenzene **(3)**. The formation of ethylbenzene may involve acid catalyzed disproportionation of **(8)** into **(3)** and $PhCH_2CHO$ **(6)** by hydride transfer: under these conditions **(6)** is expected to yield mainly polymeric products. The formation of benzene **(1)** may occur by ipsoprotonation of **(8)** forming the intermediate **(100)** followed by elimination of ethylene oxide **(101)** (scheme 3.2.2).



Scheme 3.2.2

Phenylacetic acid (11) (Table 3.2.5). Thermal reaction in cyclohexane gives mainly dibenzyl ketone **(16)** probably via condensation to the anhydride **(105)** and rearrangement to the unstable β-keto acid intermediate **(104)**, followed by decarboxylation [52JA1515]; ketone **(16)** could also be formed via the reaction of anion **(103)** with phenylacetic acid **(11)** under loss of water. Another important reaction mode is simple decarboxylation of anion **(102)** to yield toluene **(2)** (scheme 3.2.3). Interestingly, traces of benzaldehyde and methyl benzoate are also formed. In aqueous solution, the formations of toluene **(2)** and of dibenzyl ketone **(16)** are strongly inhibited. In water alone very little reaction takes place (99.8% recovery). Pyridine present in aqueous solution catalyses the decarboxylation to toluene, but no dibenzyl ketone **(16)** is observed. The decarboxylation probably involves the formation of $PhCH_2^-$ **(103)** which in water gives only toluene, but in cyclohexane also forms dibenzyl ketone.



Scheme 3.2.3

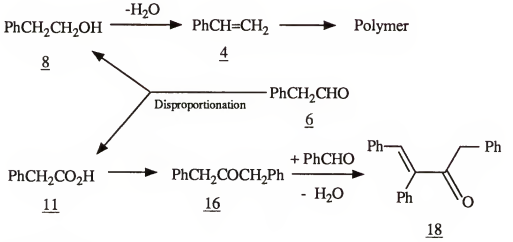
Phenylacetaldehyde (6) (Table 3.2.5). This compound is highly reactive, and 36% conversion occurs in water at 100°C for 1 day. Under these conditions two major pathways are observed:

i) disproportionation, leading to products (**4**), (**8**), (**11**), and (**18**), and

ii) aldol condensation, giving compounds (**5**), (**7**), (**13**), (**14**), (**17**), and (**19**).

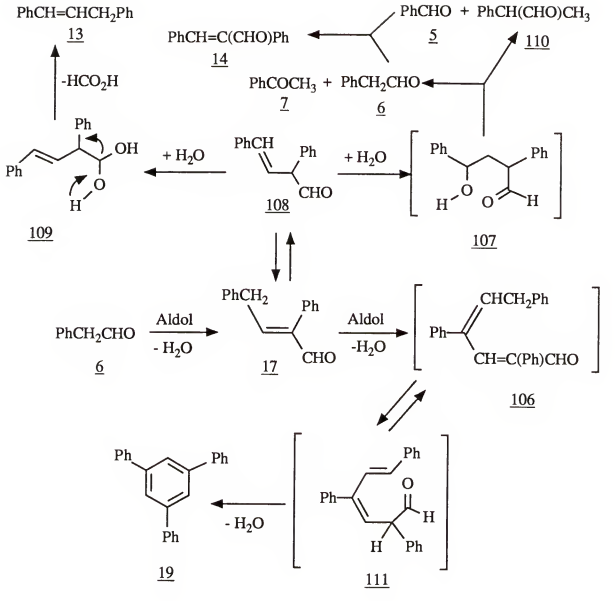
Disproportionation of phenylacetaldehyde (**6**) gives phenylethyl alcohol (**8**) and phenylacetic acid (**11**). Product (**18**) is probably formed via aldol reaction of dibenzyl ketone (**16**) with benzaldehyde (**5**) (see schemes 3.2.3 and 3.3.5). Dehydration of (**8**) leads to styrene (**4**), which under these conditions polymerizes to high molecular weight

products. Benzoic acid (**10**) is also present, and may be formed through partial disproportionation of benzaldehyde [31DRP1]. Simple decarboxylation of phenylacetic acid (**11**) gives toluene (**2**) (see also scheme 3.2.3).

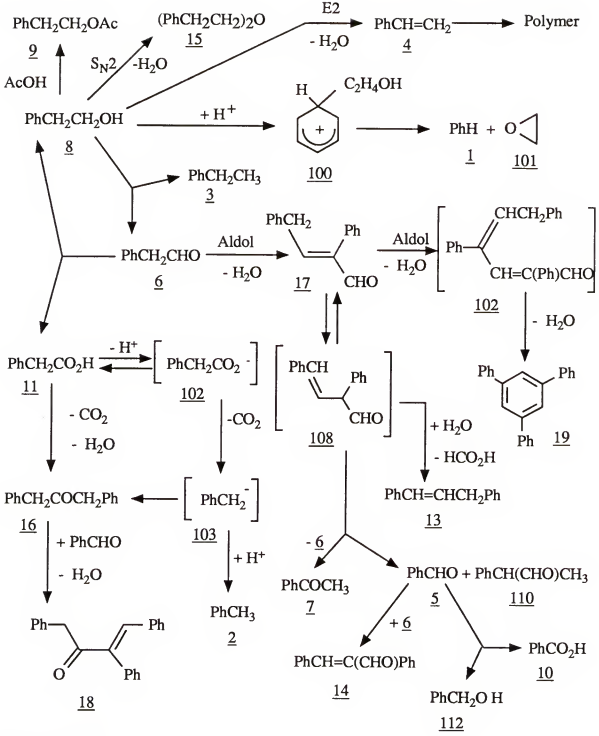


Scheme 3.2.4

The initial aldol product (**17**) undergoes further aldol condensation to (**106**) which then ring closes with loss of water to form triphenylbenzene (**19**) via the intermediate (**111**) [25BCG2607]. Rearrangement of the double bond in (**17**) to (**108**) followed by the addition of water leads to the reactive intermediates (**107**) and (**109**). Cleavage of formic acid from (**109**) gives 1,3-diphenylpropene (**13**), whereas (**107**) decomposes to give either acetophenone (**7**) and phenylacetaldehyde (**6**), or benzaldehyde (**5**) and phenylisopropylaldehyde (**110**), as side products. Product (**14**) is then generated via aldol condensation of (**6**) and (**7**).


PhCH=CHCH2Ph
13
-HCO2H
PhCH=C(CHO)Ph
14
PhCHO + PhCH(CHO)CH3
5
110
PhCOCH3 + PhCH2CHO
7
6
Ph
OH
Ph
O
H
109
+ H2O
PhCH
Ph
CHO
108
+ H2O
Ph
Ph
O
H
O
H
107
PhCH2CHO
6
Aldol
- H2O
PhCH2
Ph
CHO
17
Aldol
-H2O
CHCH2Ph
Ph
CH=C(Ph)CHO
106
Ph
Ph
Ph
19
- H2O
Ph
O
Ph
H
H
Ph
111

Scheme 3.2.5


PhCH2CH2OAc
9
AcOH
SN2
-H2O
(PhCH2CH2)2O
15
E2
- H2O
PhCH=CH2
4
Polymer
PhCH2CH2OH
8
+ H+
H
C2H4OH
100
PhH + O
1
101
PhCH2CH3
3
PhCH2CHO
6
Aldol
- H2O
PhCH2
Ph
CHO
17
Aldol
- H2O
CHCH2Ph
Ph
CH=C(Ph)CHO
102
- H2O
PhCH2CO2H
11
- H+
PhCH2CO2 -
102
- CO2
- H2O
-CO2
PhCH
Ph
CHO
108
+ H2O
- HCO2H
Ph
Ph
Ph
19
PhCH2COCH2Ph
16
+ PhCHO
- H2O
PhCH2 -
103
+ H+
PhCH=CHCH2Ph
13
- 6
PhCOCH3
7
PhCHO + PhCH(CHO)CH3
5
110
+ 6
PhCH=C(CHO)Ph
14
PhCO2H
10
PhCH2O H
112
PhCH3
2
Ph
Ph
O
Ph
18

Scheme 3.2.6

Table 3.2.1 Structure and Identification of Starting Materials and Products.

No	R_t[min]	Structure	Mol. wt.	Equiv. wt.	Ident. Basis*	Response Factor
1	0.28	Ph-H	78	78	T3	1.09
2	0.58	$PhCH_3$	92	92	T3	1.12
3	1.18	$PhCH_2CH_3$	106	106	T3	0.96
4	1.40	$PhCH=CH_2$	104	104	T2	0.96
5	1.97	PhCHO	106	106	T3	0.64
6	2.96	$PhCH_2CHO$	120	120	T2	0.62
7	3.35	PhCOMe	120	120	T2	0.75
8	3.96	$PhCH_2CH_2OH$	122	122	T2	0.71
9	6.10	$Ph(CH_2)_2OCOCH_3$	164	164	T4	0.64
10	7.16	$PhCO_2H$	122	122	T3	0.51
11	7.65	$PhCH_2CO_2H$	136	136	T2	0.38
12	9.11	PhCH=CHPh -(E)	180	180	T3	0.83
13	11.17	$PhCH=CHCH_2Ph$	194	194	T4	0.92
14	12.32	Ph(CHO)C=CHPh	208	208	T4	0.59
15	12.18	$(PhCH_2CH_2)_2O$	226	226	T4	0.72
16	12.32	$PhCH_2COCH_2Ph$	210	210	T4	0.75
17	13.04	$PhCH_2CH=C(Ph)CHO$	222	222	T4	0.58
18	17.70	$PhCH=C(Ph)COCH_2Ph$	298	298	T4	0.71
19	19.21	1,3,5-Triphenylbenzene	306	306	T3	0.88

* T2= Table 3.2.2, T3= Table 3.2.3, T4= Table 3.2.4

Table 3.2.2 Properties of Authentic Compounds Used as Starting Materials and for the Identification of Products.

No	Compound	MW	Original Source[a]	Original Purity	Purified Method	Purified Purity	m/z (% rel. intensity)	Ref.[b]
				%		%		
4	$PhCH{=}CH_2$	104	A	98.72	-	-	104(100); 103(39); 78(27); 77(14); 51(10)	108
6	$PhCH_2CHO$	120	A	98.60	-	-	120(23); 91(100); 65(20); 51(15); 39(18)	191
7	PhCOMe	120	F	98.60	dist.	99.45	120(31); 105(100); 77(70); 51(23); 43(15)	191
8	$PhCH_2CH_2OH$	122	M	99.90	-	-	122(29); 92(57); 91(100); 65(18); 39(12)	200
11	$PhCH_2CO_2H$	136	K	99.60	-	-	136(33); 91(100); 65(16); 51(5); 39(12)	4089

[a]A= Aldrich, F= Fisher, K= Kodak, M= Mallinckrodt,

[b]Heller, S.R.; Milne, G.W. EPA/NIH Mass Spectral Data Base, NBS, 1978-80 (page no.)

Table 3.2.3 Identification of Products by Comparison of Mass Spectral Fragmentation with Literature Data.

No	Compound	MW	Fragmentation found	Ref.[b]	Fragmentation reported
			m/z (% rel. intensity)	page no.	m/z (% rel. intensity)
1	PhH	78	78(100); 52(18); 51(18); 50(17); 39(16)	80	78(100); 52(21); 51(19); 50(17); 39(18)
2	$PhCH_3$	92	92(95); 91(100); 63(33); 51(21); 39(70)	850	92(93); 91(100); 63(21); 51(24); 39(45)
3	$PhCH_2CH_3$	106	106(36); 91(100); 77(8); 51(13); 39(7)	112	106(30); 91(100); 77(8); 51(12); 39(9)
5	PhCHO	106	106(98); 105(99); 77(100); 51(50); 50(25)	4018	106(42); 105(41); 77(80); 51(100); 50(47)
10	$PhCO_2H$	122	122(98); 105(100); 77(64); 51(32); 50(10)	4051	122(90); 105(100); 77(74); 51(39); 50(<1)
12	PhCH=CHPh	180	180(99); 179(100); 178(62); 165(88); 89(25)	921	180(100); 179(100); 178(70); 165(45); 89(30)
16	$PhCH_2COCH_2Ph$	210	210(8); 119(18); 118(13); 91(100); 65(23)	1040	210(8); 119(20); 118(12); 91(100); 65(23)
19	(see Table 3.2.1)	306	307(24); 306(100); 289(17); 228(17); 202(8)	1912	307(23); 306(100); 289(16); 228(16); 202(4)

[b]Heller, S.R.; Milne, G.W. EPA/NIH Mass Spectral Data Base, NBS, 1978-80 (page no.)

Table 3.2.4 Identification of Products from Mass Spectral Fragmentation Patterns.

No	Compound	MW	Fragmentation Pattern, m/z [(% rel. intensity), structure of fragment ion]
9	$Ph(CH_2)_2OAc$	164	164(3, M); 105(23, $PhC_2H_4^+$); 104(60, M-60); 91(29, $PhCH_2^+$); 43(100, $COCH_3^+$)
13	$PhCH{=}CCH_2Ph$	194	194(100, M); 193(55, M-1); 179(41, M-CH_3^+); 115(64, M-PhH^+); 91(30, $PhCH_2^+$)
14	$Ph(CHO)C{=}CHPh$	208	208(100, M); 207(53, M-1); 179(48, M-CHO); 178(71, M-CH_2O); 51(59, $C_4H_3^+$)
15	$(PhCH_2CH_2)_2O$	226	226(8, M); 208(18, M-18); 105(100, $PhC_2H_4^+$); 91(12, $PhCH_2^+$); 77(11, Ph^+)
17	$PhCH_2CH{=}C(Ph)CHO$	222	222(100, M); 221(37, M-1); 204(53, M-18); 193(13, M-CHO); 91(50, $PhCH_2^+$)
18	$PhCH{=}C(Ph)COCH_2Ph$	298	298(38, M); 207(8, M-$PhCH_2$); 193(24, M-PhCO); 129(22); 91(100, $PhCH_2^+$)

Table 3.2.5 Products [mole%] of Phenylacetaldehyde (**7**), Phenylethanol (**10**) and Phenylacetic acid (**14**).

	Compound	$PhCH_2CHO$ (7)				$PhCH_2CH_2OH$ (10)				$PhCH_2CO_2H$ (14)		
	Solvent	H_2O	C_6H_{12}	H_2O	C_6H_{12}	H_2O	H_2O	H_2O	C_6H_{12}	H_2O	H_2O	C_6H_{12}
	Additive	-	-	-	-	-	AcOH	PyH	-	-	PyH	-
	Temp.[°C]	100	100	250	250	250	250	250	250	250	250	250
	Time [days]	1	1	5	5	5	5	5	5	5	5	5
No	Structure											
1	PhH	-	-	-	-	0.1	2.0	-	-	-	-	-
2	$PhCH_3$	-	-	0.5	0.9	0.1	0.1	-	0.4	0.1	0.3	0.6
3	$PhCH_2CH_3$	-	-	-	-	0.1	1.1	0.1	0.6	-	-	-
4	$PhCH{=}CH_2$	-	-	-	0.1	1.0	0.2	2.8	1.8	-	-	-
5	PhCHO	1.5	1.2	5.1	6.4	-	-	-	-	0.1	0.2	0.1
6	$PhCH_2CHO$	67.4	82.9	19.8	19.2	-	-	-	-	-	-	-
7	PhCOMe	0.3	0.2	0.7	0.6	-	-	-	-	-	-	-
8	$PhCH_2CH_2OH$	-	-	2.6	0.6	98.9	73.3	93.4	93.2	-	-	-
9	$Ph(CH_2)_2OAc$	-	-	-	-	-	18.2	-	-	-	-	-
10	$PhCO_2H$	-	-	1.0	-	-	-	-	-	-	-	-
11	$PhCH_2CO_2H$	-	-	16.1	-	-	-	-	-	99.9	99.2	88.6
12	PhCH=CHPh-(E)	-	-	-	-	-	-	-	-	-	0.3	-
13	$PhCH{=}CHCH_2Ph$	-	-	2.5	3.7	-	-	-	-	-	-	-
14	Ph(CHO)C=CHPh	-	-	4.0	-	-	-	-	-	-	-	-
15	$(PhCH_2CH_2)_2O$	-	-	-	-	0.1	2.6	-	4.0	-	-	-
16	$PhCH_2COCH_2Ph$	-	-	-	-	-	-	-	-	-	-	10.7
17	$PhCH_2CH{=}C(CHO)Ph$	20.8	4.0	9.6	30.5	-	-	-	-	-	-	-
18	$PhCH{=}C(Ph)COCH_2Ph$	-	-	5.1	2.7	-	-	-	-	-	-	-
19	$1,3,5\text{-}Ph_3C_6H_3$	-	-	7.5	-	-	-	-	-	-	-	-
high MW products		10.0	11.6	25.4	35.4	-	2.6	3.9	-	-	-	-

3.3 Oxygenated at the Side Chain α-Position

3.3.1 Assignments of Structures

The structures of the products (**15**), (**16**), (**19**) to (**21**), (**23**) to (**28**), (**31**), (**34**), (**36**), (**37**), (**39**), (**41**), and (**42**) were deduced from their mass spectra (Table 3.3.4).

1-ß-Phenylethylcyclohexane (**15**) displays the expected fragment ions at m/e 105 (loss of C_6H_{11}), m/e 91 ($C_7H_7^+$ tropylium) and m/e 77 (Ph^+) together with an important peak at m/e 92 which is formed by proton transfer to give toluene [67MI1(e), 66TL2183].

1-Cyclohexyl-3- phenylprop-1-ene (**16**) displays a molecular ion peak at m/e 200, and a base peak at m/e 118 (C_9H_{10}), which results from the loss of cyclohexene.

Compound (**18**) is probably 1-phenyl-1-(p-ethylphenyl)ethane and exhibits a base peak at m/e 105 ($C_8H_9^+$), formed through cleavage of a p-methylbenzyl radical. The molecular ion peak expected at m/e 210 was too weak to be observed.

α-Phenylvinylcyclohexane (**19**) shows its molecular ion at m/e 186 and a loss of C_6H_{10} (cyclohexene) to give a styrene radical cation at m/e 104 which is also the base peak [67MI1(f), 65JOC331]. The loss of C_4H_9 gives a fragment at m/e 129.

Compound (**20**) is probably 1,2-dimethyl-1,2-diphenylethane and shows a base peak at m/e 105. In addition to isomer (**18**) a fragment at m/e 104 is observed, formed through the loss of phenylethane. The molecular ion peak at m/e 210 was again too weak to be observed.

1-Ethyl-2-(α-methylbenzyl)benzene (**21**), gives fragment ions at m/e 195 (loss of CH_3), m/e 181 (loss of C_2H_5), m/e 105 ($PhC_2H_5^+$) and m/e 91 ($C_7H_7^+$ tropylium). The base peak is the fragment at m/e 117 ($C_9H_9^+$) [67MI1(f)].

1,3-Diphenylbutane (**23**) shows the expected fragments m/e 91 ($C_7H_7^+$ tropylium)

and m/e 105 ($PhC_2H_5^+$), the latter is also the base peak. Important peaks at m/e 92 ($C_7H_8^{\cdot+}$) and m/e 106 ($C_8H_{10}^{\cdot+}$) arise from proton transfers via McLafferty type rearrangements [63MI1].

1-(α-Phenylethyl)-2-ethylbenzene (**24**) displays the fragment ion m/e 195 (M - CH_3), which is also the base peak. The fragment at m/e 181 results from the loss of C_2H_5 and fragment at m/e 105 is $PhC_2H_5^+$. The fragment m/e 165 probably arises via a rearrangement of m/e 181 to a tetrahydrophenanthrene (m/e 180) and loss of a methyl radical [66JCS(C)1955]

1,3-Diphenyl-2-methylbutan-1-one (**25**) displays the molecular ion peak at m/e 224, and a base peak at m/e 106 ($PhCHO^+$). Additional fragment ions are observed at m/e 119 ($PhC_3H_6^+$), m/e 105 ($PhCO^+$),and m/e 91 ($C_7H_7^+$ tropylium).

(E)-1-Methyl-1,3-diphenylpropan-1-ene (**26**) exhibits a molecular ion peak at m/e 208, and a base peak at m/e 91 ($C_7H_7^+$ tropylium). The fragment at m/e 130 results from the loss of PhH. The fragment at m/e 115 ($C_9H_7^+$) is of lesser intensity than in the isomeric structure (**31**).

1,4-Diphenylbutan-1-yne (**27**) shows the molecular ion peak at m/e 208. In addition it displays fragments at m/e 116 ($PhCH{=}C{=}CH_2^{\cdot+}$), m/e 115 ($PhCOCCH_2^+$), and m/e 91 ($C_7H_7^+$ tropylium) which is also the base peak.

1,3-Diphenylpropene (**28**) shows the molecular ion peak at m/e 194. The base peak is found at m/e 115 ($PhCH{=}CHCH_2^+$). The fragment at m/e 179 may result from a rearrangement to a phenanthrene radical cation via expulsion of a methyl radical. The peak at m/e 91 ($C_7H_7^+$ tropylium) is also present [66JCS(C)1955].

1-Methyl-1,3-diphenylpropan-1-ene (**31**) exhibits a molecular ion peak at m/e 208 and displays a similar fragmentation as its isomer (**26**) (Table 3.3.3). The base peak is at m/e 115 ($C_9H_7^+$), but the fragments m/e 193 (M - CH_3) and m/e 91 ($C_7H_7^+$ tropylium) are now of lesser intensity.

Compounds (**34**), (**36**) and (**37**) are styrene trimer isomers (probably triphenylhexene isomers). All the isomers exhibit a molecular ion peak at m/e 312, and a base peak at m/e 91 ($C_7H_7^+$ tropylium). The loss of a PhCH·Me radical results in a peak at m/e 207 ($C_{16}H_{15}^+$). The fragment m/e 207 looses PhH, to form a fragment at m/e 129 ($C_{10}H_9^+$). Another major fragment is found at m/e 117 ($PhCH{=}CH\text{-}CH_2^+$).

1,2-Benzoylethane (**39**) shows a molecular ion peak at m/e 238, and a base peak at m/e 105 ($PhCHO^+$). Other fragments are observed at m/e 77 (Ph^+) and m/e 55 ($C_4H_7^+$).

The styrene tetramer isomers (**41**) and (**42**) show almost identical spectra. Compounds (**41**) and (**42**) both exhibit very weak molecular ions at m/e 416. Both give a strong peak at m/e 117 ($PhCH^+CH{=}CH_2$), and the base peak is at m/e 91 ($C_7H_7^+$ tropylium).

3.3.2 Discussion of Results

The overall product slate and proposed reaction pathways are shown in Scheme 3.3.7 (with the exception of certain products formed in cyclohexane by the intervention of the solvent). Schemes 3.3.1 - 3.3.6 deal with proposed reaction mechanisms which are discussed under the individual starting materials.

Phenylacetylene (**3**) (Table 3.3.5). In cyclohexane, phenylacetylene reacts to the extent of about 2% after 6 hrs. at 150°C, but is completely consumed after 5 days at 250°C. The major products are 1-phenylnaphthalene (**32**), 2-phenylnaphthalene (**33**), and triphenylbenzene isomers (**35**), (**38**) and (**40**). Together these account for some 75% of the total product at the higher temperature. Other compounds formed include the reduction product ethylbenzene (**2**) and at the lower temperature some styrene (**4**), the cleavage product toluene (**1**), and the cyclohexane addition products (**15**) and (**19**). At higher temperature a large number of high molecular weight products gave an

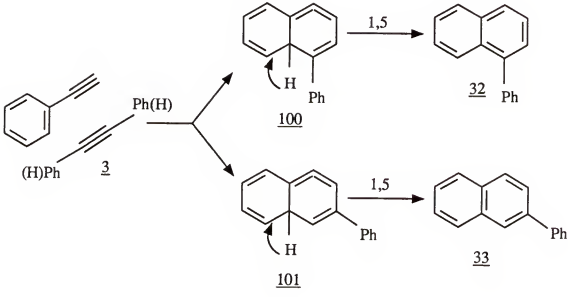
unresolved peak which accounted for about 10% of the whole. In aqueous solution, 8% of phenylacetylene reacts in 6 hrs at 150°C, but at 250°C 54% conversion is obtained. The product slate formed in water is very similar to that found in cyclohexane. Cycloaddition reactions are predominant in cyclohexane, whereas the addition of water is the major reaction under aqueous conditions. The products formed from phenylacetylene thus derive from

i) cycloadditions (compounds **32**, **33**, **35**, **38** and **40**),

ii) reduction and cleavage (compounds **1**, **2**, **4** and **22**),

iii) addition of water (**10**), and

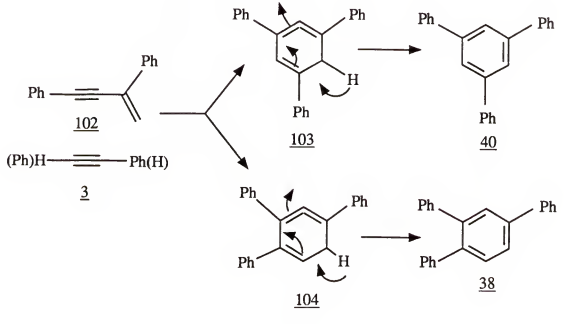
iv) addition of cyclohexane (**15** and **19**).



Scheme 3.3.1

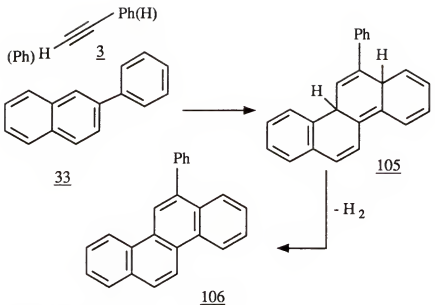
1-Phenyl- (**32**) and 2-phenyl-naphthalene (**33**) are the products of intramolecular 'ene-yne' cycloaddition reactions [63TL1234, 66T1797, 71JOC3740] between phenylacetylene via 1,5-H shifts in the allenic intermediate (**100**), (**101**) (scheme 3.3.1) [87JA578].

The triphenylbenzene isomers **(38)** and **(40)** are formed through a Diels-Alder type reaction of the phenylacetylene dimer **(102)**, with another molecule of phenylacetylene via allenic intermediates **(103)** and **(104)**, respectively (scheme 3.3.2) [87JA578, 61JOC5155,5157]. The formation of 1,2,3-triphenylbenzene **(35)** must involve the rearrangement of a phenyl group, perhaps via **(104)**.



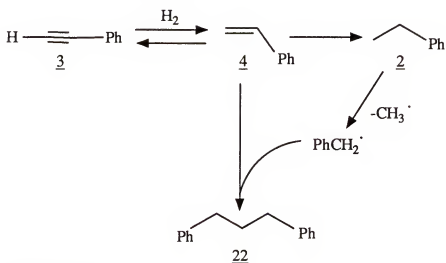
Scheme 3.3.2

The addition of hydrogen leads to styrene **(4)** and ethylbenzene **(2)**. A possible source of this hydrogen arises from Diels-Alder condensations of products such as **(33)** or **(40)** to give compounds, e.g. **(105)**, with "excess" hydrogen. Derivative **(106)** would be a component of the unresolved peaks of higher molecular weight that we found (scheme 3.3.3) [80JA3163,3173].



Scheme 3.3.3

We believe that the formation of toluene (**1**) and 1,3-diphenyl-propane (**22**) involves the homolytic cleavage of ethylbenzene (**2**) to produce a benzyl radical, which then reacts further to form (**1**), or adds to styrene to give (**22**) (scheme 3.3.4),.



Scheme 3.3.4

The simple addition of water to phenylacetylene to give acetophenone (**10**) is well known [68JOC845]. Cyclohexane addition products (**15**) and (**18**) are probably formed by hydrogen atom transfer from cyclohexane to (**3**), followed by combination of the two radicals.

Styrene (**4**) (Table 3.3.5). The only product isolated after aquathermolysis at 250°C for 5 days was polystyrene. Under the same reaction conditions, polymerization seems to be inhibited in cyclohexane, where the major products are dimers, trimers and tetramers of styrene together accounting for 60% of the products. About 8% of the styrene remains unreacted. After 6 hrs at 150°C in cyclohexane, only 1% of the styrene has reacted, but under these conditions in aqueous solution 46% was converted to polystyrene. The products from styrene thus derive from

i) complete polymerization to polystyrene in aqueous solution,

ii) dimers (**26, 30, 31**) trimers (**34, 36, 37**) and tetramers (**41, 42**) are formed in cyclohexane, and

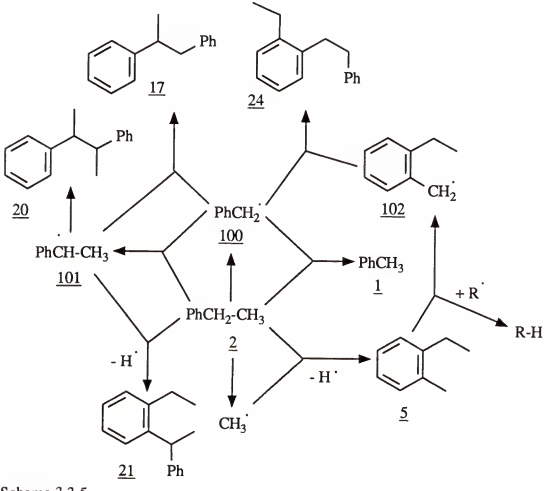
iii) products of reductive cleavage (**2, 22**).

The polymerization in water probably proceeds through an acid catalyzed cationic mechanism. In cyclohexane, acid catalysis may be caused by trace amounts of water, or by the acidic surface of the glass liner, but it is far less effective and thus leads only to oligomers. Styrene dimers, trimers, and tetramers are frequently referrred to in the literature [68JA1289, 69MA130, 77JOC3477]. However, structural information about the various trimer and tetramer isomers is scarce. Mayo reported a 2,4,6-triphenyl-hexan-1-ene [68JA1289], Brown [69MA130], and Kurze et al. [70AG(E)537] reported a 1-phenyl-4-(1-phenethyl)-1,2,3,4tetrahydronaphthalene. Hydrogen for reduction can arise from processes similar to scheme 3.3.3 discussed above, and this then produces ethylbenzene (**2**). Homolytic cleavage of (**2**) forms benzyl and methyl radicals which then allows formation of ortho-ethyltoluene (**5**) and 1,3-di-phenylpropane (**22**).

Ethylbenzene (2) (Table 3.3.5). Reaction is very slow, but after 21 days at 250°C ca. 1% conversion is observed both in cyclohexane and in aqueous solution. Reaction is somewhat slower in the presence of either pyridine or phosphoric acid.

i) The formation of $PhCH_3$ (**1**), of $PhCH_2CHMePh$ (**17**) and of $Ph(CHMe)_2$ (**20**) suggests that homolytic fission occurs giving $PhCH_2^{\cdot}$ and $PhCH^{\cdot}Me$ radicals as intermediates (scheme 3.3.5).

ii) Acetophenone (**10**) is formed in H_2O only in the presence of acid or base catalysis, probably via $PhCH^+CH_3$.



Scheme 3.3.5

α-Phenylethanol **(11)** (Table 3.3.6). In water at 250°C only 17% reacted after 1 day, but no α-phenylethanol was detected after 5 days. The situation shows similarities to benzyl alcohol [89EF5ip], and suggests that the reactions are ionic, even in cyclohexane where the rapid loss of water provides a relatively polar environment. The proposed reaction mechanism is outlined in scheme 3.3.6. The first key intermediate is the α-phenylethyl cation **(107)** which reacts with another molecule **(11)** in a dispro-portionation reaction to yield acetophenone **(10)** and ethylbenzene **(2)**. Reaction of $PhCH^+CH_3$ **(107)** with styrene gives the second key intermediate cation $PhCH^+CH_2CH(Ph)Me$ **(108)**. Cation **(108)** is

i) reduced by **(11)** to $EtC_6H_4CH_2CH_2Ph$-ortho **(24)**,

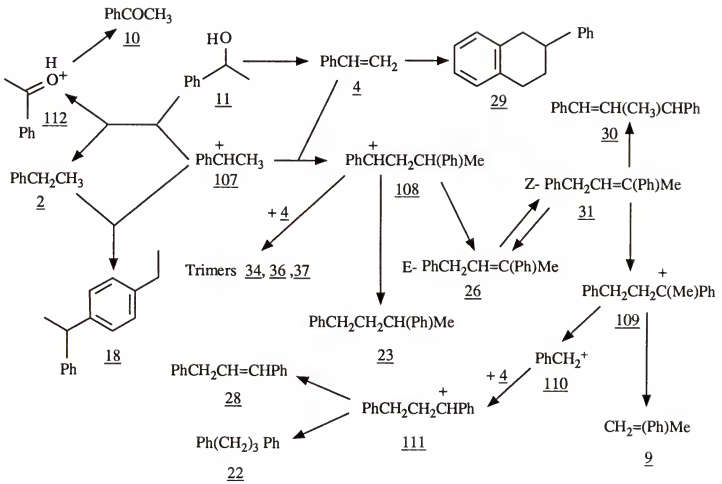
ii) deprotonated at alternating positions to form styrene dimers **(26, 30, 31)**,

iii) added to more styrene in alternating ways to give styrene trimers **(34)**, **(36)** and **(37)**, and

iv) isomerizes to the third key intermediate, cation **(109)**.

Cation **(109)** in turn undergoes scission to $PhCH_2CH{=}CH_2$ **(9)** and benzyl cation **(110)**. Benzyl cation **(110)** adds to styrene to form **(111)** which is deprotonated to **(22)** or reduced to **(28)**.

Acetophenone **(10)** (Table 3.3.7). Reaction rates are much slower than for the corresponding alcohol in both H_2O and cyclohexane, with just 1% and 2.5% conversion after 5 days at 250°C, respectively. Moreover, after 14 days at 250°C in aqueous solution with an equimolar amount of H_3PO_4, only 6% conversion was obtained; 2% triphenylbenzene **(40)** was the major product, which suggests an Aldol-type condensation. With acetic acid as additive after 5 days at 250°C, 8% of acetophenone is converted, of which isopropylbenzene **(7)** accounts for 4%. The reaction pathways are


PhCOCH3
10
H
O+
Ph
112
HO
Ph
11
PhCH=CH2
4
Ph
29
PhCH=CH(CH3)CHPh
30
PhCH2CH3
2
+
PhCHCH3
107
+
PhCHCH2CH(Ph)Me
108
Z- PhCH2CH=C(Ph)Me
31
+ 4
Trimers 34, 36 ,37
E- PhCH2CH=C(Ph)Me
26
+
PhCH2CH2C(Me)Ph
109
Ph
18
PhCH2CH2CH(Ph)Me
23
PhCH2+
110
+ 4
PhCH2CH=CHPh
28
+
PhCH2CH2CHPh
111
CH2=(Ph)Me
9
Ph(CH2)3 Ph
22

Scheme 3.3.6

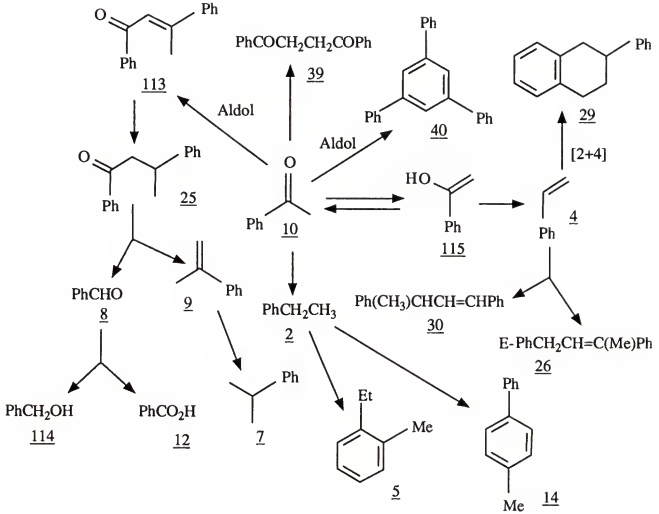
i) aldol condensation leading to 1,3,5-triphenylbenzene (**40**) and to the key intermediate (**25**) formed through the condensation of two molecules of acetophenone to give (**113**) followed by reduction, and

ii) the reduction of acetophenone (**10**) to styrene (**4**).

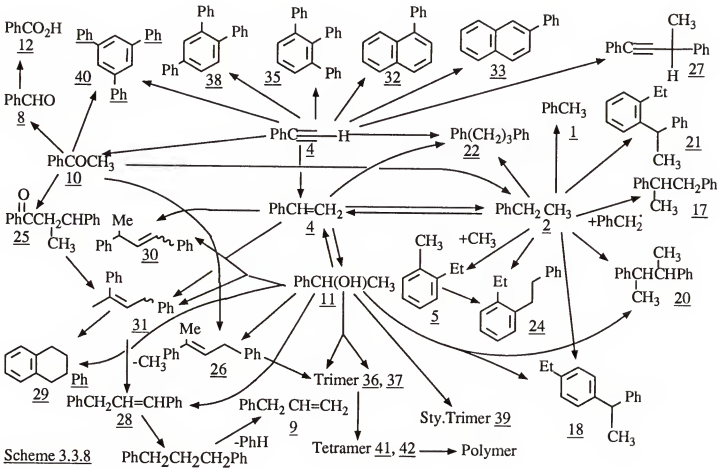
Thermal cleavage of compound (**25**) via a McLafferty type fragmentation leads to benzaldehyde (**8**) and phenylisopropene (**9**), which then is hydrated to isopropylbenzene (**7**). Benzaldehyde disproportionates to benzyl alcohol (**114**) and benzoic acid (**12**). The diketone (**39**) may result from a radical coupling (scheme 3.3.7).

Styrene (**4**) formed via the reduction of acetophenone (**10**), adds hydrogen to form ethylbenzene (**2**). Styrene then dimerizes to give (**26**) and (**30**), and 2-phenyltetrahydronaphthalene (**29**) which is probably formed via a Diels Alder addition [69MA130, 77JOC3477].

Ethylbenzene (**2**) undergoes homolytic cleavage and reacts further to give the products (**14**) and (**5**).


O
Ph
Ph
113
PhCOCH2CH2COPh
39
Aldol
Aldol
Ph
Ph
Ph
40
Ph
29
[2+4]
O
Ph
25
O
Ph
10
HO
Ph
115
Ph
4
PhCHO
8
9
Ph
PhCH2CH3
2
Ph(CH3)CHCH=CHPh
30
E-PhCH2CH=C(Me)Ph
26
PhCH2OH
114
PhCO2H
12
Ph
7
Et
Me
5
Ph
Me
14

Scheme 3 .3 .7


PhCO2H 12
PhCHO 8
PhCOCH3 10
PhC≡CH 4
PhCH=CH2 4
PhCH2CH3 2
PhCH(OH)CH3 11
PhCH2CH=CHPh 28
PhCH2CH2CH2Ph
PhCH2CH=CH2 9
Trimer 36, 37
Sty.Trimer 39
Tetramer 41, 42
Polymer
-PhH
-CH3
+CH3
+PhCH2
Ph(CH2)3Ph 22
PhCH3 1
PhCHCH2Ph CH3 17
PhCHCHPh CH3 20
PhCH2CHCHPh 25
40
38
35
32
33
27
21
30
31
26
29
5
24
18

Scheme 3.3.8

Table 3.3.1 Structure and Identification of Starting Materials and Products.

No	R_t[min]	Structure	Mol. wt.	Equiv. wt.	Ident. Basis*	Response Factor
1	0.62	$PhCH_3$	92	92	T3	1.12
2	1.04	$PhCH_2CH_3$	106	106	T2	0.96
3	1.22	$PhC{\equiv}CH$	102	102	T2	0.95
4	1.28	$PhCH{=}CH_2$	104	104	T2	0.96
5	1.53	MeC_6H_4Et-ortho	120	120	T3	0.95
6	1.81	$PhCH_2CHO$	120	120	T3	0.62
7	1.83	$PhCH(CH_3)_2$	120	120	T3	0.95
8	1.97	PhCHO	106	106	T3	0.64
9	2.09	$PhCH_2CH{=}CH_2$	118	118	T3	0.95
10	2.97	PhCOMe	120	120	T2	0.75
11	3.23	$PhCH(OH)CH_3$	122	122	T2	0.78
12	7.16	$PhCO_2H$	122	122	T2	0.51
13	7.76	$PhCH_2Ph$	168	84	T3	0.85
14	8.52	$C_6H_4(Me)Ph$	168	84	T3	0.93
15	8.99	$PhCH_2CH_2C_6H_{11}$	188	188	T4	0.93
16	9.62	1-Cyclohexyl-3-phenylprop-1-ene	200	200	T4	0.91
17	9.75	$PhCH_2CH(CH_3)Ph$	196	98	T3	0.92
18	9.90	1-Phenyl-1-(p-ethylphenyl)ethane	210	105	T4	0.92
19	9.94	$Ph(C_6H_{11})C{=}CH_2$	186	186	T4	0.93
20	10.08	1,2-Dimethyl-1,2-diphenylethane	210	105	T4	0.92
21	10.43	$PhCH(CH_3)C_6H_4Et$-ortho	210	105	T4	0.92

Table 3.3.1 cont.

No	R_t[min]	Structure	Mol. wt.	Eqiv. wt.	Ident. Basis	Response Factor
22	10.45	$Ph(CH_2)_3Ph$	196	98	T3	0.92
23	10.83	$PhCH(CH_3)CH_2CH_2Ph$	210	105	T4	0.92
24	10.84	$EtC_6H_4CH_2CH_2Ph$-ortho	210	105	T4	0.92
25	10.84	$PhCOCH_2CH(CH_3)Ph$	224	112	T4	0.74
26	11.25	$PhCH_2CH{=}C(CH_3)Ph$-(E)	208	104	T4	0.92
27	11.31	$PhC{\equiv}CCH_2CH_2Ph$	206	103	T4	0.91
28	11.32	1,3-Diphenylpropene	194	97	T4	0.91
29	11.49	Tetrahydro-2-Ph-naphthalene	208	104	T3	0.92
30	11.84	$PhCH{=}CHCH(CH_3)Ph$	208	104	T3	0.92
31	12.09	$PhCH_2CH{=}C(CH_3)Ph$	208	104	T4	0.92
32	12.56	1-Phenylnaphthalene	204	102	T3	0.92
33	13.62	2-Phenylnaphthalene	204	102	T3	0.92
34	17.47	Styrene Trimer	312	104	T4	0.88
35	17.55	1,2,3-Triphenylbenzene	306	102	T3	0.88
36	18.00	Styrene Trimer	312	104	T4	0.88
37	18.93	Styrene Trimer	312	104	T4	0.88
38	19.80	1,2,4-Triphenylbenzene	306	102	T3	0.88
39	20.80	$PhCOCH_2CH_2COPh$	238	117	T4	0.57
40	21.58	1,3,5-Triphenylbenzene	306	102	T3	0.88
41	23.51	Styrene Tetramer	416	104	T4	0.85
42	23.68	Styrene Tetramer	416	104	T4	0.85

*T2= Table 3.3.2, T3= Table 3.3.3, T4= Table 3.3.4

Table 3.3.2 Properties of Authentic Compounds Used as Starting Materials and for the Identification of Products.

No	Compound	MW	Original Source[a]	Original Purity	Purified Method	Purified Purity	m/z (% rel. intensity)	Lit. Ref.[b]
				%		%		
2	$PhCH_2CH_3$	106	F	99.60	-	-	106(64); 91(100); 77(11); 65(20); 57(17)	112
3	PhC_2H	102	A	98.50	-	-	102(100); 76(13); 74(29); 63(17); 50(32)	100
4	$PhCH=CH_2$	104	F	99.00	-	-	104(100); 103(39); 78(27); 77(14); 51(10)	108
6	$PhCH_2CHO$	120	A	98.60	-	-	120(23); 91(100); 65(20); 51)15); 39(19)	191
10	PhCOMe	120	F	98.60	dist.	99.45	120(31), 105(100), 77(70), 51(23), 43(15)	191
13	$PhCH(OH)CH_3$	122	Fl	99.80	-	-	122(13); 107(52); 79(100); 78(59); 51(74)	242

[a]A=Aldrich, F=Fisher, K=Kodak, M=Mallinckrodt, Fl=Fluka

[b]Heller, S.R.; Milne, G.W. EPA/NIH Mass Spectral Data Base, NBS, 1978-80 (page no.)

Table 3.3.3 Identification of Products by Comparison of Mass Spectral Fragmentation with Literature Data.

No	Compound	MW	Fragmentation found		Fragmentation reported
			m/z (% rel. intensity)	Ref.	m/z (% rel. intensity)[b]
1	$PhCH_3$	92	92(72); 91(100); 63(30); 51(16); 39(55)	57	92(73); 91(100); 65(13); 51(11); 39(20)
5	MeC_6H_4Et-o	120	120(27); 105(100); 91(20); 77(43); 39(51)	192	120(30); 105(100); 91(11); 77(10); 39(11)
7	$PhCH(CH_3)_2$	120	120(32); 105(100); 91(8); 89(2); 77(15)	4049	120(28); 105(100); 91(18); 98(10); 77(12)
8	PhCHO	106	106(98); 105(99); 77(100); 51(50); 50(52)	4018	106(42); 105(41); 77(80); 51(100); 50(47)
9	$PhCH_2CH{=}CH_2$	118	118(100); 117(77); 103(42); 63(36); 51(68)	185	118(100); 117(72); 103(47); 63(20); 51(72)
12	$PhCO_2H$	122	122(98); 105(100); 77(64); 51(32); 50(10)	4051	122(90); 105(100); 77(74); 51(39); 50(<1)
13	$PhCH_2Ph$	168	168(98); 167(100); 165(60); 152(31); 91(88)	740	168(100); 167(95); 165(33); 152(21); 91(21)
14	MeC_6H_4Ph-p	168	168(100); 167(19); 165(28); 152(13); 65(10)	740	168(100); 167(48); 165(22); 152(19); 65(12)
17	(see Table 3.3.1)	196	196(<1); 105(100); 104(20); 103(17); 77(23)	1137	196(3); 105(100); 104(16); 103(6); 77(13)
22	$Ph(CH_2)_3Ph$	196	196(54); 105(36); 92(70); 91(100); 65(49)	1137	196(37); 105(52); 92(100); 91(67); 65(18)
29	(see Table 3.3.1)	208	208(55); 104(100); 103(19); 78(12); 77(12)	1289	208(48); 104(100); 103(13); 78(15); 77(10)
30	(see Table 3.3.1)	208	208(82); 193(50);; 178(20); 115(100); 91(37)	1298	208(96); 193(95); 178(31); 115(100); 91(41)
32	(see Table 3.3.1)	204	204(100);203(74); 202(41); 201(19); 101(32)	1243	204(100); 203(77); 202(53); 101(34); 8(11)
33	(see Table 3.3.1)	204	204(100); 203(23); 202(33); 201(19); 101(20)	1243	204(100); 203(18); 202(30); 101(10); 89(8)
35	(see Table 3.3.1)	306	307(19); 306(100); 305(30); 290(23); 289(24)	2309	307(25); 306(100); 305(31); 290(18); 289(25)
38	(see Table 3.3.1)	306	307(28); 306(100); 203(8); 202(14); 145(9)	2309	307(28); 306(100); 203(31); 202(30); 145(5)
40	(see Table 3.3.1)	306	307(27); 306(100); 289(9); 228(12); 226(9)	2309	307(28); 306(100); 289(5); 228(6); 226(5)

[b]Heller, S.R.; Milne, G.W. EPA/NIH Mass Spectral Data Base, NBS, 1978-80 (page no.)

Table 3.3.4 Identification of Products from Mass Spectral Fragmentation Patterns

No	Compound	MW	Fragmentation Pattern, m/z [(% rel. intensity), structure of fragment ion]
15	$PhCH_2CH_2C_6H_{11}$	188	188(30 M^+); 92(98, $C_7H_8^+$); 91(100, $PhCH_2^+$); 65(50, $C_6H_5^+$); 55(52, $C_4H_7^+$)
16	(see Table 3.3.1)	200	200(37, M^+); 118(100, M - C_6H_{10}); 115(35, $C_9H_7^+$); 55(44, $C_4H_9^+$); 39(40, $C_3H_3^+$)
18	(see Table 3.3.1)	210	210(<1 M^+); 121(19, M - $C_5H_5^{\cdot}$); 106(16, M - C_8H_{10}); 105(100, $C_8H_9^+$); 77(24, Ph^+)
19	$Ph(C_6H_{11})C{=}CH_2$	186	186(90, M^+); 129(37, M - $C_4H_9^{\cdot}$); 128(44, M - C_4H_{10}); 115(55, $C_9H_7^+$); 104(100, $C_8H_8^+$)
20	(see Table 3.3.1)	210	210(<1, M^+); 105(100, $C_8H_9^+$); 104(20, $C_8H_8^+$); 79(16, $C_6H_7^+$); 77(20, Ph^+)
21	$PhCH(CH_3)C_6H_4Et$-o	210	210(53, M^+); 195(78, M-CH_3); 117(100, $C_9H_9^+$); 105(75, $C_8H_9^+$); 91(84, $PhCH_2^+$)
23	$PhCH(CH_3)C_2H_4Ph$	210	210(42, M^+); 105(100, $C_8H_9^+$); 91(90, $PhCH_2^+$); 79(40, $C_6H_9^+$); 77(53, Ph^+)
24	(see Table 3.3.1)	210	210(82, M^+); 195(100, M - CH_3); 178(51, $C_{14}H_{10}$); 165(61, $C_{13}H_9^+$); 105(81, $C_8H_9^+$)
25	$PhCOCH_2CH(CH)_3Ph$	224	224(13, M^+); 119(21, M - PhCO); 106(100, PhCHO); 105(98, $PhCO^+$); 91(62, $PhCH_2^+$)
26	$PhCH_2CH{=}C(CH_3)Ph$-E	208	208(21, M^+); 130(28, M - C_6H_6); 115(30, $C_9H_7^+$); 91(100, $PhCH_2^+$); 65(55, $C_5H_5^+$)
27	$PhC{\equiv}CCH_2CH_2Ph$	206	206(18, M^+); 116(54, C_9H_8); 115(100, $C_9H_7^+$); 91(48, $PhCH_2^+$); 65(69, $C_5H_5^+$)
28	$PhCH_2CH{=}CHPh$	194	194(57, M^+); 179(17, M - CH_3); 178(25, $C_{14}H_{10}$); 116(50, C_9H_8); 115(100, $C_9H_7^+$)
31	$PhCH_2CH{=}C(CH_3)Ph$-Z	208	208(58, M^+); 193(28, M - CH_3); 130(29, M - PhH); 115(100, $C_9H_7^+$); 91(53, $PhCH_2^+$)
34	(see Table 3.3.1)	312	312(14, M); 207(66, M - PhC_2H_4); 129(55, $C_{10}H_9^+$); 91(100, $PhCH_2^+$); 77(17, Ph^+)
36	(see Table 3.3.1)	312	312(13, M); 207(21, M - PhC_2H_4); 117(66, $PhCH{=}CHCH_2^+$); 103(11, $PhC_2H_2^+$); 91(100, $PhCH_2^+$)
37	(see Table 3.3.1)	312	312(30, M); 207(67, M - PhC_2H_4); 129(79, $C_{10}H_9^+$); 117(28, $PhCH{=}CHCH_2^+$); 91(100, $PhCH_2^+$)
39	$PhCOCH_2CH_2COPh$	238	238(5, M^+); 106(9, PhCHO); 105(100, $PhCO^+$); 77(35, Ph^+); 55(12, $C_4H_7^+$)
41	(see Table 3.3.1)	416	416(<1, M^+); 298(4, M - $C_9H_{10}^{\cdot}$); 193(7, 298 - $PhC_2H_5^{\cdot}$); 117(40, $PhC_3H_4^+$); 91(100, $C_7H_7^+$)
42	(see Table 3.3.1)	416	416(<1, M^+); 298(4, M - $C_9H_{10}^{\cdot}$); 193(6, 298 - $PhC_2H_5^{\cdot}$); 117(39, $PhC_3H_4^+$); 91(100, $C_7H_7^+$)

Table 3.3.5 Products [mole%] of Phenylacetylene (3) and Styrene (4) Reactions.

		PhC≡CH				PhCH=CH$_2$			
	Solvent	H_2O	H_2O	C_6H_{12}	C_6H_{12}	H_2O	H_2O	C_6H_{12}	C_6H_{12}
	Additive	-	-	-	-	-	-	-	-
	Temp.[^oC]	150	250	150	250	150	250	150	250
	Time [days]	0.25	5	0.25	5	0.25	5	0.25	5
No	Structure								
1	$PhCH_3$	-	0.1	-	2.2	-	-	-	-
2	$PhCH_2CH_3$	-	0.3	-	3.6	-	-	-	0.4
3	PhC≡CH	91.6	-	97.8	-	-	-	-	-
4	$PhCH=CH_2$	0.7	0.3	0.8	-	51.0	-	99.0	6.6
5	o-MeC_6H_4Et	-	-	-	-	-	-	-	0.4
10	PhCOMe	1.3	50.8	-	-	-	-	-	-
13	$PhCH_2Ph$	-	0.4	-	1.1	-	-	-	-
15	$PhCH_2CH_2(C_6H_{11})$	-	-	-	1.9	-	-	-	-
19	$Ph(C_6H_{11})C=CH_2$	-	-	-	3.0	-	-	-	-
22	$Ph(CH_2)_3Ph$	-	-	-	1.0	-	-	-	1.7
26	$PhCH_2CH=C(CH_3)Ph$-E	-	-	-	-	-	-	-	12.9
27	$PhC≡CCH_2CH_2Ph$	-	-	-	1.8	-	-	-	-
30	$PhCH=CHCH(CH_3)Ph$	-	-	-	-	-	-	-	0.5
31	$PhCH_2CH=C(CH_3)Ph$-Z	-	-	-	-	-	-	-	2.0
32	1-Phenylnaphthalene	3.9	17.4	1.0	28.1	-	-	-	-
33	2-Phenylnaphthalene	0.1	1.4	-	10.5	-	-	-	-
34	Styrene Trimer	-	-	-	-	-	-	-	0.6
35	1,2,3-Triphenylbenzene	0.3	2.6	0.1	4.7	-	-	-	-
36	Styrene Trimer	-	-	-	-	-	-	-	42.6
37	Styrene Trimer	-	-	-	-	-	-	-	5.2
38	1,2,4-Triphenylbenzene	1.0	9.6	0.1	17.5	-	-	-	-
40	1,3,5-Triphenylbenzene	2.1	16.4	0.1	17.4	-	-	-	-
41	Styrene Tetramer	-	-	-	-	-	-	-	9.8
42	Styrene Tetramer	-	-	-	-	-	-	-	9.0
41	Polystyrene	-	-	-	-	48.0	100.0	-	-
Unresolved peaks		0.1	1.1	0.1	7.3	1.0	-	1.0	8.5

Table 3.3.6 Products [mole%] of Ethylbenzene (**2**) and α-Phenylethanol (**11**) Reactions

		$PhCH_2CH_3$				$PhCH(OH)CH_3$			
	Solvent	H_2O	H_2O	H_2O	C_6H_{12}	H_2O	H_2O	C_6H_{12}	C_6H_{12}
	Additive	-	PyH	H_3PO_4	-	-	-	-	-
	Temp.[°C]	250	250	250	250	250	250	250	250
	Time [days]	21	5	5	21	1	5	1	5
No	Structure								
1	$PhCH_3$	0.3	0.3	0.3	0.3	-	-	-	-
2	$PhCH_2CH_3$	98.9	99.3	99.0	98.6	0.2	8.2	0.2	3.5
4	$PhCH{=}CH_2$	-	-	-	-	4.6	5.0	21.5	35.2
5	o-MeC_6H_4Et	-	-	0.1	0.1	-	-	-	-
6	$PhCH_2CHO$	-	-	-	0.1	-	-	-	-
9	$PhCH_2CH{=}CH_2$	-	-	-	-	0.1	6.5	0.1	0.7
10	$PhCOCH_3$	0.3	0.4	0.1	0.4	2.3	43.5	2.0	18.3
11	$PhCH(OH)CH_3$	-	-	-	-	86.7	-	61.2	-
15	$PhCH_2CH_2(C_6H_{11})$	-	-	-	-	-	-	-	0.2
16	$PhCH_2CH{=}CH\text{-}C_6H_{11}$	-	-	-	-	-	-	-	0.4
17	$PhCH_2CH(CH_3)Ph$	0.2	-	-	0.1	-	-	-	-
18	(see Table 3.3.1)	-	-	-	-	1.7	-	4.5	4.4
20	(see Table 3.3.1)	-	-	-	0.1	2.4	-	2.9	6.2
21	$PhCH(CH_3)C_6H_4Et$-o	-	-	0.1	-	-	-	-	-
22	$Ph(CH_2)_3Ph$	-	-	-	-	-	1.9	0.1	1.1
23	$PhCH(CH_3)C_2H_4Ph$	-	-	-	-	-	6.6	-	1.3
24	$EtC_6H_4CH_2CH_2Ph$-o	-	-	0.1	-	-	-	-	-
26	Styrene Dimer	-	-	-	-	0.3	1.5	0.7	2.6
28	$PhCH_2CH{=}CHPh$	-	-	-	-	-	3.0	-	-
29	Tetra-H-2-Ph-naphthalene	-	-	-	-	0.1	-	0.4	2.3
30	$PhCH{=}CHCH(CH_3)Ph$	-	-	-	-	0.2	8.8	1.0	5.3
31	$Ph(CH_3)C{=}CHCH_2Ph$	-	-	-	-	-	10.1	-	1.9
34	Styrene Trimer	-	-	-	-	-	-	-	0.8
36	Styrene Trimer	-	-	-	-	0.9	3.0	4.2	16.1
37	Styrene Trimer	-	-	-	-	-	2.0	-	4.1
Unresolved peaks		0.4	0.1	0.4	0.3	0.5	-	1.3	4.2

Table 3.3.7 Products [mole%] of Acetophenone (**10**) Reactions.

		$PhCOCH_3$					
	Solvent	H_2O	H_2O	H_2O	H_2O	H_2O	C_6H_{12}
	Additive	-	AcOH	PyH	PyH	H_3PO_4	-
	Temp.[°C]	250	250	250	250	250	250
	Time [days]	5	5	5	14	14	5
No	Structure						
2	$PhCH_2CH_3$	0.1	1.0	<0.1	-	0.2	0.1
5	o-MeC_6H_4Et	-	-	-	0.2	0.5	-
7	$PhCH(CH_3)_2$	0.1	2.5	0.2	-	-	0.2
8	PhCHO	0.1	1.1	-	-	-	-
9	$PhCH_2CH{=}CH_2$	-	-	-	-	0.2	-
10	PhCOMe	98.4	94.1	98.9	99.8	95.7	98.5
12	$PhCO_2H$	-	-	0.3	-	-	-
14	$C_6H_4(Me)Ph$	0.1	0.1	0.1	-	-	-
25	$PhCOCH_2CH(CH_3)Ph$	-	0.1	-	-	0.2	-
26	Styrene Dimer	-	-	-	-	0.2	-
29	Tetra-H-2-Ph-naphthalene	-	-	-	-	0.3	-
30	$CH_3(Ph)C{=}C(CH_3)Ph$	-	-	-	-	0.2	-
39	$PhCOCH_2CH_2COPh$	-	0.5	-	-	-	-
40	1,3,5-Triphenylbenzene	-	-	-	-	1.5	-
Unresolved peaks		1.2	0.6	0.5	-	1.1	1.3

3.4 Oxygenated at the Side Chain α- and β-Positions

3.4.1 Assignment of Structures

The structures of the products (**3**), (**15**), (**18**), (**21 - 25**), and (**27 - 32**) were deduced from their electron impact mass spectra (Table 3.4.4). The mass spectra of compounds (**3**), (**18**), (**21**), (**27**), (**29**), (**31**), and (**32**) were obtained under chemical ionization (CI) conditions with CH_4 as ionization gas. Under CI conditions $(M + 1)^+$ and $(M + 29)^+$ peaks are frequently encountered, as is to be expected [78AG(E)424].

Cyclohexane carboxaldehyde (**3**) shows a $(M + 1)^+$ peak at m/e 113, and a $(M + 29)^+$ peak at m/e 141. The base peak is found at m/e 95, which results from a loss of water from the protonated molecular ion. A fragment at m/e 83 ($C_6H_{11}^+$) is also observed.

Phenylcyclohexyl ketone (**15**) displays the molecular ion at m/e 188 and the base peak at m/e 105 ($PhCO^+$). Fragments deriving from the aromatic ring, m/e 77 (Ph^+), 51 ($C_4H_3^+$) and m/e 39 ($C_3H_3^+$), were also observed.

1-Phenyl-2-cyclohexyl-1,2-ethanedione (**18**) shows the $(M + 1)^+$ peak at m/e 217 and a $(M + 29)^+$ peak at m/e 245. Loss of water from the $(M + 1)^+$ fragment leads to a peak at m/e 199. The expected fragments [67MI1(g)] for an α-diketone, at m/e 111 ($C_6H_{11}CO^+$) and at m/e 105 ($PhCO^+$), which is also the base peak, are present.

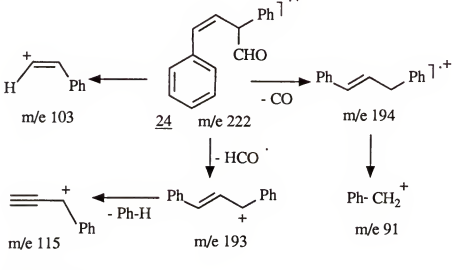
Cyclohexyl benzoylformate (**21**) exhibits a $(M + 1)^+$ peak at m/e 233 in the CI spectrum. The base peak, found at m/e 151, is formed via loss of cyclohexene (-82) from the protonated molecular ion. The fragments at m/e 191 and m/e 177

are formed probably through loss of C_4H_8 and C_3H_6 from the $(M + 1)^+$ ion, respectively. The expected fragment at m/e 105 ($PhCO^+$) is also observed.

α-Phenylcinnamic acid **(22)** shows an intense molecular ion peak at m/e 224. The base peak at m/e 178 is formed through loss of formic acid. The loss of m/e 45 (CO_2H), typical for acids [67MI1(h)], leads to the fragment at m/e 179.

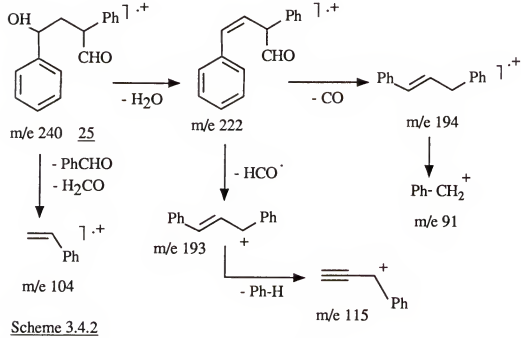
2,4-Diphenylbutanal-3-ol **(23)** displays a ($m^+ - 1$) peak, typical for alcohols [67MI1(i)], at m/e 239. The base peak is observed at m/e 121 ($PhCH_2CH^+OH$). Loss of $PhCH_2^{\cdot}$ from the molecular ion forms the fragment at m/e 149 [PhCH(CHO)CH^+OH]. The fragment at m/e 103 is formed via loss of water, and following cleavage of a PhCH(CHO)$^{\cdot}$ radical. The molecular ion at m/e 240 could not be observed.

2,4-Diphenylbutanal-3-ene **(24)** gives fragment ions at m/e 91 ($C_7H_7^+$ tropylium), m/e 103 ($PhCH{=}CH^+$), and m/e 115 ($PhCH^+COCH$, or a cyclized form). The molecular ion is displayed at m/e 222, and is also the base peak (scheme 3.4.1).



Scheme 3.4.1

2,4-Diphenylbutanal-4-ol (**25**) shows the molecular ion peak at m/e 240, and the base peak at m/e 115 ($PhCH^+COCH$). Loss of water gives the fragment m/e 222. Cleavage of benzaldehyde and formaldehyde forms the styrene radical cation at m/e 104. A fragment at m/e 91 ($C_7H_7^+$ tropylium) is also found.



Scheme 3.4.2

1,3-Diphenylbutan-3-ol-1-one (**27**) exhibits the fragments $(M + 29)^+$ at m/e 269 and $(M + 1)^+$ at m/e 241. The fragment at m/e 121 is probably $PhC^+(OH)CH_3$. The base peak is the fragment at m/e 105 ($PhCO^+$).

Compound (**28**) is probably diphenylmaleic acid anhydride with a molecular ion peak at m/e 250, and a base peak at m/e 178, formed through loss of CO and CO_2.

1,4-Diphenyl-4-hydroxy-1,3-butanedione (**29**) shows the $(M + 1)^+$ peak at m/e 255 and a base peak at m/e 137 [$PhCH(OH)CH^+OH$]. Additional fragments

are found at m/e 121 [PhC(OH)Me$^+$], m/e 105 (PhCO$^+$), and m/e 91 ($C_7H_7^+$ tropylium).

2,5-Diphenylfuran-3-one **(30)** displays its molecular ion peak at m/e 236. The base peak is m/e 105 (PhCO$^+$). Loss of CO gives the fragment m/e 208. Cleavage of a PhCO· radical results in a fragment t m/e 131.

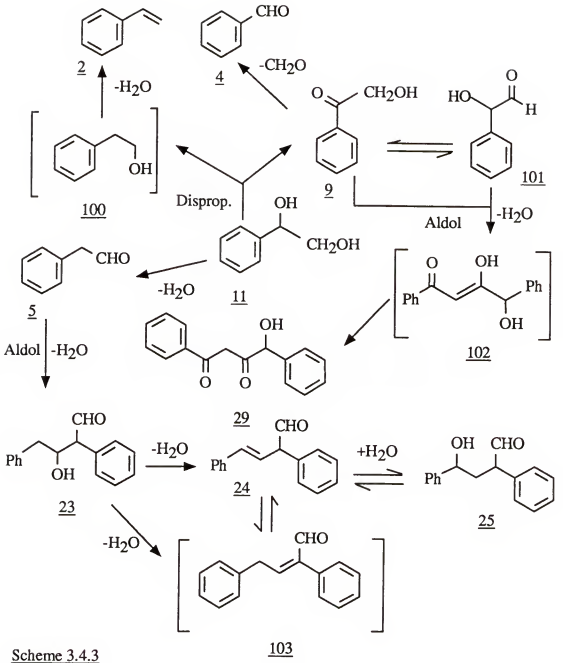
4,5-Dihydro-2,5-diphenylfuran-3-one **(31)** in the CI mass spectrum shows a $(M + 1)^+$ peak at m/e 239 which is also base peak. Loss of benzene gives a fragment at m/e 161. Other peaks are found at m/e 121 [PhCH(OH)CH_2]$^+$, and 105 (PhCO$^+$).

1,4-Diphenylbutan-2-ol-1,3,4-trione **(32)** exhibits its $(M + 1)^+$ peak at m/e 269, and the base peak at m/e 105 (PhCO$^+$). Loss of CO gives the fragment at m/e 241.

3.4.2 Discussion of Results

The overall product slate, and proposed reaction pathways are shown in scheme 3.4.7 (with the exception of certain products formed in cyclohexane by the intervention of the solvent). Schemes 3.4.3 - 3.4.6 deal with proposed reaction mechanisms which are discussed under the individual starting materials.

Phenylethane-1,2-diol **(11)** (Table 3.4.5). At 200°C for 6 hrs. in water, phenylethanediol is consumed to the extent of 90%, whereas under the same conditions in cyclohexane the conversion is only 14%. The major products in water are phenylacetaldehyde **(5)** (24%) [45JA518] and the condensation product **(24)** of **(5)**. In cyclohexane, benzoylcarbinol **(9)**, and the addition product **(23)** formed from phenylacetaldehyde, were also found. According to the reaction


2
-H2O
4
-CH2O
CHO
O
CH2OH
HO
O
H
OH
100
Disprop.
9
101
Aldol
-H2O
OH
CH2OH
CHO
-H2O
11
5
O
OH
Ph
Ph
OH
Aldol -H2O
102
OH
O
O
29
CHO
CHO
Ph
OH
-H2O
Ph
+H2O
OH
CHO
Ph
23
24
25
-H2O
CHO
103

Scheme 3.4.3

mechanisms of scheme 3.4.3, the products formed from phenylethane diol are postulated to derive from

i) dehydration (compound **5**),

ii) disproportionation initially to (**100**) which yields (**2**), and (**9**) which reacts further to (**4**), and

iii) aldol condensation of (**5**) to give (**23 - 25**) and of (**9**) to give (**29**).

The rate of consumption of the starting material in water is approximately seven times faster than in cyclohexane. This may be explained by the stabilizing effect of the more polar solvent water, on the transition state leading to dehydration of (**11**). After protonation, the α-hydroxy group of (**11**) leaves as water, assisted by the ß-hydroxyl, to give the enol of phenylacetaldehyde (**5**). Compound (**23**) is formed via a aldol condensation of (**5**), and dehydration of (**23**) gives the unsaturated compound (**24**). In cyclohexane, (**11**) gives an oxidized product, benzoylcarbinol (**9**), and a trace of a reduced product, styrene (**2**), which may arise from phenethyl alcohol. In water only traces of (**9**) could be detected; (**9**) is probably a precursor of the benzaldehyde (**5**), formed via cleavage of formaldehyde.

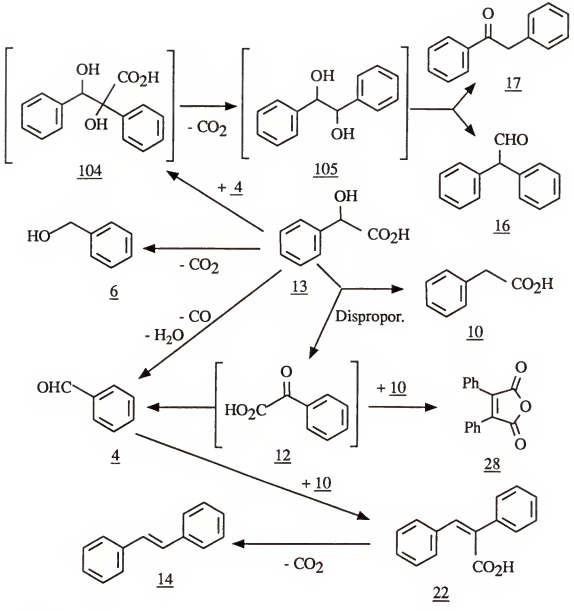
Mandelic acid (**13**) (Table 3.4.5). At 200°C for 6 hrs., mandelic acid (**13**) shows a slightly higher conversion in cyclohexane as solvent than in water. The overall conversion in water is 2%, compared to 10% in cyclohexane. The only product formed in water under these conditions is benzaldehyde (**4**), via loss of ($CO + H_2O$) a well known reaction [33JA1541, 06BCG51, 1886BCG638]. In cyclohexane the major products are phenylacetic acid (**10**) and benzaldehyde (**4**). The major reaction pathways are

i) decarboxylation (compound **6**),

ii) cleavage of CO and water (compound **4**),

iii) disproportionation (compound **10**), and

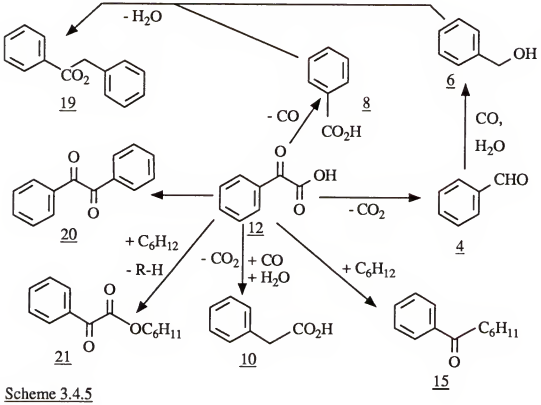
iv) addition, condensation and oxidation (compounds **14**, **17** and **22**).



Scheme 3.4.4

Almost complete conversion is found at 250°C for 24 hrs. in water as well as in cyclohexane as solvent. The major products are benzaldehyde **(4)** and phenylacetic acid **(10)** which account for 66% of the products in water and 87% in cyclohexane. The cinnamic acid derivative **(22)** is probably formed via the addition of benzaldehyde **(4)** to the 'acid enolate' of phenylacetic acid **(10)**. Decarboxylation of **(22)** leads to stilbene **(14)**. The formation of benzyl alcohol **(6)** can take place either via direct decarboxylation of mandelic acid **(13)** or via a reduction of benzaldehyde **(4)** with formic acid ($CO + H_2O$) [89EF5ip].

Benzoylformic acid **(12)** (Table 3.4.6). The overall conversion at 200°C for 4 hrs. is 2% in water, and 6% in cyclohexane. The major reaction products are benzaldehyde **(4)**, and benzoic acid **(8)** [34JA1348].



Scheme 3.4.5

After 24 hrs. at 200°C complete conversion takes place in either solvent. In water, 87% benzaldehyde (**4**) and 9% benzoic acid (**8**) is formed, but only 59% benzaldehyde is formed in cyclohexane, along with 10% benzoic acid and 21% benzoin (**20**).

The major reaction pathways are suggested to be those in scheme 3.4.5

i) decarboxylation (compound **4**),

ii) decarbonylation (compound **8**),

iii) reduction (compound **10**), and

iv) reactions with cyclohexane (compounds **15**, and **21**).

Simple decarboxylation of (**12**) gives benzaldehyde (**4**), and decarbonylation leads to benzoic acid (**8**), both are well known reactions [1877BCG1666, 57Ag483, 56HCA548]. Only small amounts of benzyl alcohol (**6**) are found in cyclohexane, whereas in water 2% of (**6**) is formed. In water benzyl alcohol (**6**) is probably formed by reduction with CO, formed in the reaction (**12**) → (**4**). Earlier aquathermolysis experiments with benzaldehyde, alone and with formic acid as additive, show that formic acid increases the benzyl alcohol formation to 30% [89EF5ip]. Compounds (**15**) and (**21**) are formed via radical mechanisms. The reduction of the α-carbonyl group of (**12**) leads to the formation of phenylacetic acid (**10**). At 200°C for 24 hrs. in cyclohexane, small amounts of stilbene (**14**), and the ester (**19**) are also formed. Benzoin (**20**) is a major product only in cyclohexane, which suggests a non ionic mechanism.

Phenylglyoxal hydrate (**7**) (Table 3.4.6). Phenylglyoxal (**7**) is the most reactive compound in this series. Complete conversion is found at 200°C, after only 2 hrs., in both water and cyclohexane. However, no reaction occured at 100°C for 8 hrs. in either solvent. At 150°C for 6 hrs. the conversion was 14% in

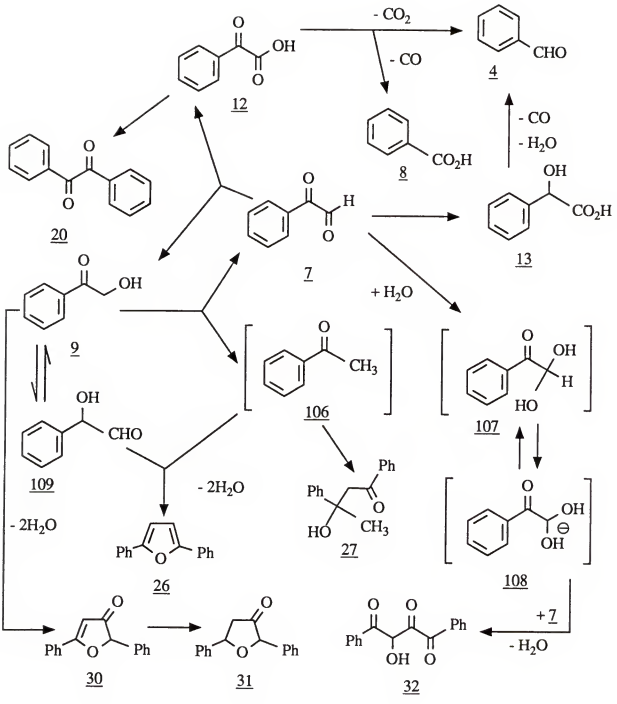
water and 34% in cyclohexane. The major reaction pathways outlined in scheme 3.4.6 are

i) rearrangement to mandelic acid (**13**)in water [57Ag483],

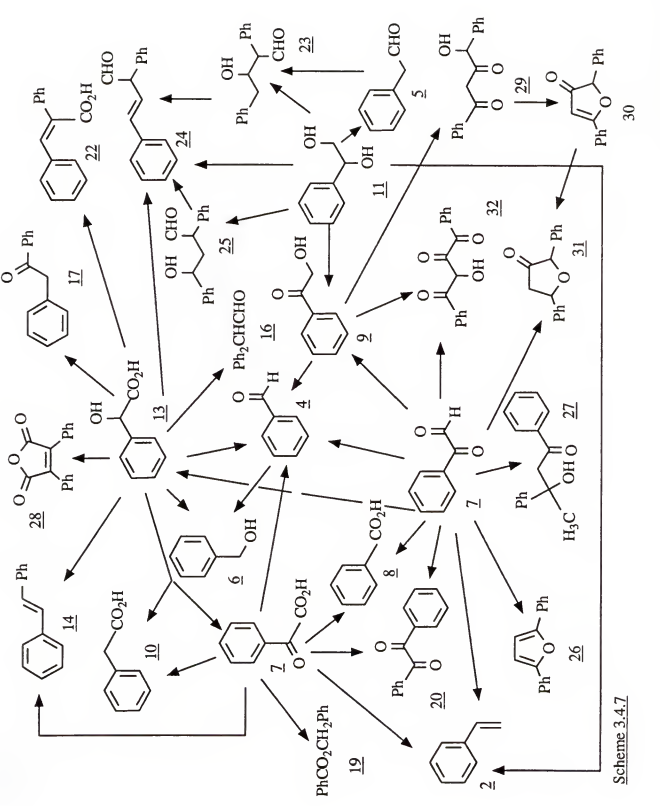
ii) disproportionation (compound **9**), and

iii) condensation (compounds **32**, and **27**).

At 150°C for 6 hrs. the only product formed in water is mandelic acid (**13**), whereas in cyclohexane compound (**32**), formed via self condensation of anion (**108**) with (**7**), and compound (**27**) which could have formed via the condensation of two molecules of (**106**), are also found (see scheme 3.4.6). Disproportionation of (**7**) to benzoylcarbinol (**9**) leads to the formation of 2,5-diphenylfuran (**26**) in water, but interestingly only to the reduced forms (**30**) and (**31**) in cyclohexane. In water at 200°C for 6 hrs. only a small amount of (**30**) is present (see scheme 3.4.6). Benzoylformic acid (**12**), the other disproportionation product, completely decomposes to benzaldehyde (**4**) and benzoic acid (**8**). Benzoin (**20**) is formed mainly in cyclohexane, with (**12**) as possible precursor.


- CO2
- CO
4
CHO
12
OH
O
8
CO2H
- CO
- H2O
OH
CO2H
13
20
7
+ H2O
9
OH
106
CH3
107
OH
H
HO
109
CHO
- 2H2O
- 2H2O
26
Ph
27
HO
CH3
108
OH
OH
+ 7
- H2O
30
31
32
OH

Scheme 3.4.6



Scheme 3.4.7

Table 3.4.1 Structure and Identification of Starting Materials and Products.

No	Rt[min]	Structure	Mol. wt.	Equiv wt.	Ident. Basis*	Response Factor
1	0.63	$PhCH_3$	92	92	T3	1.12
2	1.22	$PhCH{=}CH_2$	104	104	T3	0.96
3	1.54	$C_6H_{11}CHO$	112	112	T4	0.58
4	1.69	PhCHO	106	106	T3	0.64
5	2.69	$PhCH_2CHO$	120	120	T3	0.62
6	2.91	$PhCH_2OH$	108	108	T3	0.78
7	2.95	PhCOCHO	134	134	T2	0.45
8	5.17	$PhCO_2H$	122	122	T3	0.51
9	5.45	$PhCOCH_2OH$	136	136	T3	0.60
10	6.40	$PhCH_2CO_2H$	136	136	T3	0.38
11	6.53	$PhCH(OH)CH_2OH$	138	138	T2	0.60
12	6.63	$PhCOCO_2H$	150	150	T2	0.20
13	8.63	$PhCH(OH)CO_2H$	152	152	T2	0.20
14	9.11	PhCH=CHPh -(E)	180	90	T3	0.83
15	9.89	$PhCOC_6H_{11}$	188	188	T4	0.76
16	10.50	Ph_2CHCHO	196	98	T3	0.59
17	11.17	$PhCH_2COPh$	196	98	T3	0.75
18	11.39	$C_6H_{11}COCOPh$	216	216	T4	0.58
19	11.50	$PhCO_2CH_2Ph$	212	106	T3	0.62
20	11.98	PhCOCOPh	210	105	T3	0.58
21	2.39	$PhCOCO_2C_6H_{11}$	232	232	T4	0.45
22	13.12	$PhCH{=}C(Ph)CO_2H$	224	112	T4	0.34
23	13.29	$PhCH_2CH(OH)CH(CHO)Ph$	240	120	T4	0.40
24	13.51	PhCH=CHCH(CHO)Ph	222	111	T4	0.58
25	13.84	$PhCH(OH)CH_2CH(CHO)Ph$	240	120	T4	0.40
26	14.32	2,5-diphenylfuran	220	110	T3	0.72
27	14.53	$PhC(CH_3)(OH)CH_2COPh$	240	120	T4	0.56
28	14.81	Diphenyl maleic acid anhydride	250	125	T4	0.38
29	15.55	$PhCOCH_2COCH(OH)Ph$	254	127	T4	0.39
30	15.58	2,5-Diphenylfuran-3-one	236	118	T4	0.55
31	16.34	4,5-Dihydro-2,5-diphenylfuran-3-one	238	119	T4	0.55
32	18.13	PhCOCH(OH)COCOPh	268	134	T4	0.22

*T2= Table 3.4.2, T3= Table 3.4.3, T4= Table 3.4.4

Table 3.4.2 Properties of Authentic Compounds Used as Starting Materials and for the Identification of Products.

No	Compound	MW	Original Source*	Original Purity	Purified Method	Purified Purity	Mass Spectra
				%		%	m/z (% rel. intensity)
7	PhCOCHO	134	A	99.00	--	--	134(<1); 105(100); 77(88); 51(70); 50(38)
8	$PhCH(OH)CO_2H$	152	A	99.00	--	--	152(6); 107(100); 105(20); 79(56); 77(4)
11	$PhCH(OH)CH_2OH$	138	A	99.34	--	--	138(10); 107(100); 105(11); 79(64); 77(46)
12	$PhCOCO_2H$	150	A	98.00	--	--	150(<1); 105(100); 77(50); 51(45); 45(20)

*A= Aldrich

Table 3.4.3 Identification of Products by Comparison of Mass Spectral Fragmentation with Literature Data.

No	Compound	MW	Fragmentation found	Ref.	Fragmentation reported[b,c]
			m/z (% rel. intensity)		m/z (% rel. intensity)
1	$PhCH_3$	92	92(72); 91(100); 63(30); 51(16); 39(55)	57[a]	92(73); 91(100); 65(13); 51(11); 39(20)
2	$PhCH=CH_2$	104	104(100); 103(38); 78(22); 77(18); 51(6)	208[a]	104(100); 103(39); 78(27); 77(14); 51(10)
4	PhCHO	106	106(98); 105(99); 77(100); 51(50); 50(25)	4018[a]	106(42); 105(41); 77(80); 51(100); 50(47)
5	$PhCH_2CHO$	120	120(27); 92(14); 91(100); 65(11); 56(6)	477[b]	120(27); 92(23); 91(100); 65(13); 56(6)
6	$PhCH_2OH$	108	108(94); 107(63); 79(100); 77(60); 51(28)	117[a]	108(79); 107(64); 79(100); 77(62); 51(45)
8	$PhCO_2H$	122	122(98); 105(100); 77(64); 51(32); 50(10)	4051[a]	122(90); 105(100); 77(74); 51(39); 50(<1)
10	$PhCH_2CO_2OH$	136	136(36); 105(5); 92(15); 91(100); 65(14)	312[a]	136(35); 105(2); 92(17); 91(100); 65(12)
14	PhCH=CHPh	180	180(99); 179(100); 178(62); 165(88); 89(25)	921[a]	180(100); 179(100); 178(70); 165(45); 89(30)
16	Ph_2CHCHO	196	196(3); 168(12); 167(100); 165(39); 152(26)	1135[a]	196(3); 168(20); 167(100); 165(32); 152(22)
17	$PhCH_2COPh$	196	196(2); 106(8); 105(100); 91(12); 77(42)	1135[a]	196(12); 106(30); 105(100); 91(19); 77(38)
19	$PhCO_2CH_2Ph$	212	212(38); 105(100); 91(58); 77(25); 51(15)	1346[a]	212(22); 105(100); 91(42); 77(30); 51(10)
20	PhCOCOPh	210	210(3); 105(100); 104(8); 77(48); 51(28)	4472[a]	210(1); 105(100); 104(X); 77(40); 51(12)
26	(see Table 3.4.1)	220	220(100); 115(28); 110(16); 105(15); 77(22)	1453[a]	220(100); 115(31); 110(16); 105(16); 77(24)

[b] Heller, S.R.; Milne, G.W. EPA/NIH Mass Spectral Data Base, NBS, 1978-1980 (page no.)

[c] Stenhagen, E.; Abrahamsson, S.; McLafferty, F.W. ; Atlas of Mass Spectral Data; Intersience Publishers, N.Y. 1969

Table 3.4.4 Identification of Products from Mass Spectral Fragmentation Patterns.

No	Compound	MW	Fragmentation Pattern, m/z [(% rel. intensity), structure of fragment ion]
3	$C_6H_{11}CHO$	112*	141(2, M^++29); 113(18, M^++1); 95(100, M^++1 - H_2O); 83(29, $C_6H_{11}^+$)
9	$PhCOCH_2OH$	136*	177(7, M^+ + 41); 165(2, M^+ + 29); 137(100, M^+ + 1); 119(51, M^+ + 1 -H_2O); 105(2, $PhCO^+$)
15	$PhCOC_6H_{11}$	188	188(13, M^+); 105(100, $PhCO^+$); 77(66, Ph^+); 51(48, C_4H_3+); 39(20, $C_3H_3^+$)
18	$PhCOCOC_6H_{11}$	216*	245(15, M^++29); 217(34, M^++1); 199(45, M^++1 - H_2O); 111(14, $C_6H_{11}CO^+$); 105(100, $PhCO^+$)
21	$PhCOCO_2C_6H_{11}$	232*	233(3, M^++1); 191(13, M^+ - $C_3H_5^+$); 177(30,M^+ - C_4H_7);151(100, $PhCOCO_2H_2^+$); 105(30, $PhCO_+$);
22	$PhCH{=}C(Ph)CO_2H$	224	224(87, M^+); 179(88, M^+ - CO_2H); 178(100, M^+ - HCO_2H); 167(18, Ph_2CH^+); 152(12, Ph_2)
23	(see Table 3.4.1)	240	240(<1, M^+); 239(23, M^+ - 1); 149(79, M^+ - $PhCH_2$·); 121(100, $PhCH_2CHOH^+$); 91(66, $PhCH_2^+$)
24	$PhCH{=}CHCH(CHO)Ph$	222	222(100, M^+); 204(12, M^+ - H_2O); 115(42, $PhCH^+COCH$); 103(20, $PhCH{=}CH^+$); 91($PhCH_2^+$)
25	(see Table 3.4.1)	240	240(10, M^+); 222(65, M^+ - H_2O); 115(100, $PhCH^+COCH$); 104(90, $PhCH{=}CH_2$); 91(73, $PhCH2^+$)
27	(see Table 3.4.1)	240*	269(21, M^+ + 29); 241(36, M^+ + 1); 145(16,); 121(15, $PhC^+(OH)CH_3$); 105(100, $PhCO^+$)
28	(see Table 3.4.1)	250	250(45, M^+); 222(22, M^+ - CO); 179(19); 178(100, M^+ - CO_2); 76(18, $C_6H_4^+$)
29	(see Table 3.4.1)	254*	255(16, M^+ + 1); 137(100, $PhCH(OH)CH^+OH$); 121(46, $PhCOHCH_3^+$); 105(32, $PhCO^+$); 91(36)
30	(see Table 3.4.1)	236	236(6, M^+); 208(3, M^+ - CO); 131(3, M^+ - 105); 105(100, $PhCO^+$); 77(56, Ph^+)
31	(see Table 3.4.1)	238*	267(14, M^+ + 29); 239(100, M^+ + 1); 161(M^+ + 1 - 78); 121(6; $PhCO^+HCH_3$); 105(6, $PhCO^+$)
32	(see Table 3.4.1)	268*	269(4, M^+ + 1); 241(9, M^+ + 1 - CO); 135(12, $PhCOCH_2O^+$); 121(27, $PhCO^+HCH_3$); 105(100, $PhCO^+$)

*=Methane Chemical Ionization

Table 3.4.5 Products [mole%] of Phenylethanediol **(11)**, Mandelic acid **(13)** and Benzoyl formic acid **(12)** Reactions.

		$PhCH(OH)CH_2OH$		$PhCH(OH)CO_2H$				$PhCOCO_2H$			
	Solvent	H_2O	C_6H_{12}	H_2O	C_6H_{12}	H_2O	C_6H_{12}	H_2O	C_6H_{11}	H_2O	C_6H_{12}
	Additive	-	-	-	-	-	-	-	-	-	-
	Temp.[°C]	200	200	200	200	250	250	200	200	200	200
	Time [hours]	6	6	6	6	24	24	4	4	24	24
No	Structure										
1	$PhCH_3$	-	-	-	-	-	-	-	-	-	0.1
2	$PhCH{=}CH_2$	-	0.2	-	-	-	-	-	0.3	-	-
4	PhCHO	0.2	-	1.9	5.8	26.0	72.2	1.7	3.9	87.3	58.8
5	$PhCH_2CHO$	24.1	1.3	-	-	-	-	-	-	-	-
6	$PhCH_2OH$	-	-	-	-	1.6	-	-	-	2.4	0.2
8	$PhCO_2H$	-	-	-	-	-	-	0.2	0.5	8.5	9.9
9	$PhCOCH_2OH$	-	0.6	-	-	-	-	-	-	-	-
10	$PhCH_2CO_2H$	-	-	-	2.9	40.4	13.4	-	-	-	0.9
11	$PhCH(OH)CH_2OH$	10.0	86.1	-	-	-	-	-	-	-	-
12	$PhCOCO_2H$	-	-	-	-	-	-	98.0	94.2	-	-
13	$PhCH(OH)CO_2H$	-	-	98.0	89.6	6.6	1.3	-	-	-	-
14	PhCH=CHPh -(E)	-	-	-	-	1.7	0.5	-	-	-	0.2
15	$PhCOC_6H_{11}$	-	-	-	-	-	-	-	0.1	-	0.1
16	Ph_2CHCHO	-	-	-	-	0.7	3.8	-	-	-	-

Table 3.4.5 cont.

		PhCH(OH)CH_2OH		PhCH(OH)CO_2H				PhCOCO_2H			
	Solvent	H_2O	C_6H_{12}	H_2O	C_6H_{12}	H_2O	C_6H_{12}	H_2O	C_6H_{11}	H_2O	C_6H_{12}
	Additive	-	-	-	-	-	-	-	-	-	-
	Temp.[^oC]	200	200	200	200	250	250	200	200	200	200
	Time [hours]	6	6	6	6	24	24	4	4	24	24
No	Structure										
17	$PhCH_2COPh$	-	-	-	-	5.9	2.4	-	-	-	-
19	$PhCO_2CH_2Ph$	-	-	-	-	-	-	-	-	-	0.3
20	PhCOCOPh	-	-	-	-	-	-	-	0.5	1.8	21.0
21	$PhCOCO_2C_6H_{11}$	-	-	-	-	-	0.4	-	0.6	-	-
22	PhCH=C(Ph)CO_2H	-	-	-	-	-	1.3	-	-	-	-
23	$PhCH_2CH(OH)CH(CHO)Ph$	9.2	3.5	-	-	-	-	-	-	-	-
24	PhCH=CHCH(CHO)Ph	41.3	1.3	-	-	0.4	-	-	-	-	-
25	$PhCH(OH)CH_2CH(CHO)Ph$	9.6	-	-	-	-	-	-	-	-	-
28	$PhCH_2CH(OH)CH_2COPh$	-	-	-	1.8	5.8	1.6	-	-	-	-
29	$PhCOCH_2COCH(OH)Ph$	4.1	-	-	-	-	-	-	-	-	-
	Unresolved peaks:	1.5	7.1	0.2	-	5.1	1.4	-	-	-	8.6

Table 3.4.6 Products [mole%] of Phenylglyoxal (**7**) Reactions.

		PhCOCHO					
	Solvent	H_2O	C_6H_{12}	H_2O	C_6H_{12}	H_2O	C_6H_{12}
	Additive	-	-	-	-	-	-
	Temp.[^{0}C]	100	100	200	200	200	200
	Time [hours]			2	2	6	6
No	Structure						
2	$PhCH{=}CH_2$	-	-	-	-	-	3.5
3	$C_6H_{11}CHO$	-	-	-	-	-	5.7
4	PhCHO	-	-	1.2	5.3	10.4	10.6
7	PhCOCHO	86.3	66.1	-	-	-	-
8	$PhCO_2H$	-	-	1.5	9.3	43.4	16.3
9	$PhCOCH_2OH$	-	-	1.0	9.7	3.3	5.5
13	$PhCH(OH)CO_2H$	13.7	-	94.9	-	-	-
18	$C_6H_{11}COCOPh$	-	-	-	-	-	4.2
20	PhCOCOPh	-	-	-	11.8	4.5	6.1
26	2,5-diphenylfuran	-	-	1.4	-	26.5	-
27	$PhCCH_3(OH)CH_2COPh$	-	8.0	-	10.6	-	20.7
29	$PhCOCH_2COCH(OH)Ph$	-	-	-	-	5.2	6.7
30	(see Table 3.4.1)	-	-	-	23.0	5.2	-
31	(see Table 3.4.1)	-	-	-	-	-	7.7
32	PhCOCH(OH)COCOPh	-	25.8	-	17.9	-	11.2
	unresolved peaks	-	-	-	12.1	1.5	1.7

3.5 Conclusions

In cyclohexane the major reactions of 2-phenylethanol are the dehydrations to form either styrene, or the ether $PhCH_2CH_2OCH_2CH_2Ph$. A smaller amount of reduction to ethylbenzene and some toluene is found. In water alone reaction is much slower and the major process is again dehydration but now much more styrene is produced. The rate of reaction in water is accelerated by pyridine, and especially by acetic acid. The last conditions give mainly 2-phenylethyl acetate but also appreciable amounts of benzene and ethylbenzene.

The thermal reaction of phenylacetic acid in cyclohexane gives mainly dibenzylketone by a Claisen type condensation followed by decarboxylation. Another important reaction mode is simple the decarboxylation to yield toluene. Interestingly, traces of benzaldehyde and methylbenzoate are formed. In aqueous solution, the formations of toluene and of dibenzylketone are strongly inhibited. In water alone very little reaction takes place (99.8% recovery). Pyridine, present in aqueous solution, catalyzes the decarboxylation to toluene, but no Claisen condensation products are observed.

Phenylacetaldehyde is highly reactive and 36% conversion occurs in water at 100°C for 1 day. Under these conditions the major conversion path is via the aldol reaction, leading to triphenylbenzene and to high boiling products (15%).

Ethylbenzene reacts very slowly, but perceptably, via the formation of $PhCH_2$· radicals. By contrast, styrene rapidly polymerizes in aqueous solution, but leads to di-, tri-, and tetramers in cyclohexane. Phenylacetylene reacts at an intermediate rate, mainly by thermal di- and trimerisation reactions.

In cyclohexane, phenylacetylene reacts to the extent of about 2% after 6 hrs. at 150°C, but is completely consumed after 5 days at 250°C. The major products are 1-phenylnaphthalene, 2-phenylnaphthalene, and triphenylbenzene isomers. Together these account for some 75% of the total product at the higher temperature. Other compounds formed include the reduction product ethylbenzene, and cyclohexane addition products. In aqueous solution, 8% of the phenylacetylene reacts in 6 hrs. at 150°C, but at 250°C 54% conversion is obtained. The product slate formed in water is very different to that found in cyclohexane. Cycloaddition reactions are predominant in cyclohexane, whereas the addition of water is the major reaction under aqueous conditions.

α-Phenylethanol decomposes quite rapidly, the major pathways are cationic; styrene is formed, but rather than polymerizing, it is captured in aqueous solution by a phenethyl cation to give di- and trimers. In water at 250°C only 17% conversion takes place after 1 day, but no α-phenylethanol is detected after 5 days. The situation shows similarities to benzyl alcohol, and suggests that the reactions are ionic, even in cyclohexane where the rapid loss of water provides a relatively polar environment.

Reaction rates for acetophenone are much slower than for the corresponding alcohol in both H_2O and cyclohexane, with just 1% and 2.5% conversion after 5 days at 250°C, respectively. Moreover, after 14 days at 250°C in aqueous solution with an equimolar amount of H_3PO_4, only 6% conversion was obtained; 2% triphenylbenzene was the major product, which suggests an aldol condensation. With acetic acid as additive, after 5 days at 250°C, 8% of acetophenone is converted, of which isopropylbenzene accounts for 4%.

Phenylethane-1,2-diol mandelic acid, benzoylformic acid, and phenylglyoxal are very reactive in both water and cyclohexane. The α- keto and α-hydroxy acids undergo

mainly decarbonylation and decarboxylation. Disproportionation products are key intermediates as precursors for condensation and cyclyzation products.

Phenylethane-1,2-diol is consumed approximately seven times faster in cyclohexane then in water. The overall conversion in water at 200°C for 6 hrs. is 90% versus 14% in cyclohexane under the same conditions.

Mandelic acid shows a five times higher conversion in cyclohexane than in water at 200°C for 6 hrs. In cyclohexane the only observed reaction pathway is the formation of benzaldehyde via loss of $CO + H_2O$. Interesting is the formation of benzyl alcohol at 250°C for 24 hrs. which may be due to the reduction of benzaldehyde by formic acid ($CO + H_2O$), or direct decarboxylation of mandelic acid.

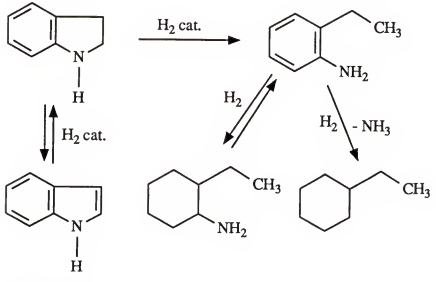
Benzoylformic acid shows a three times higher conversion in cyclohexane than in water under the same conditions at 200°C for 4 hrs. A complete conversion is achieved after 24 hrs. at 200°C in either solvent. Simple decarbonylation leads to benzoic acid, and decarboxylation to benzaldehyde as major products. Small amounts of benzyl alcohol and phenylacetic acid are also found, probably due to formic acid generated in the process.

Phenylglyoxal, the last compound in this series is also the most reactive, and shows a complete conversion at 200°C for only 2 hrs. in both solvents. In water phenylglyoxal formed almost exclusively mandelic acid, whereas no mandelic acid was found under thermal conditions.

CHAPTER 4
AQUEOUS THERMOLYSIS OF HETEROCYCLES

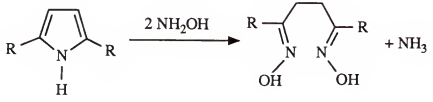
4.1 Introduction

Heterocyclic compounds are widely distributed in fossil resources. Particularly high amounts of up to 2 weight % of sulfur is found in oil shales and oil sands or coal [87MI3]. The most frequently found heterocyclic systems in fossil fuel resources are pyrroles, thiophenes, pyridines and their benzo condensed analogs, as well as porphyrins [81MI1]. One part in the upgrading process of fossil fuels is directly aimed at the removal of heteroatoms as NH_3 or H_2S, via catalytic hydrogenation [81MI2] (scheme 4.1.1).



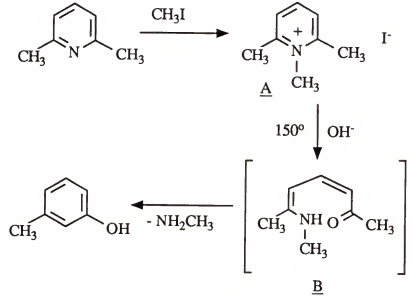
Scheme 4.1.1

Several other methods are available which lead to a ring opening of the heterocyclic molecule and eventual removal of the heteroatom. Pyrroles are known to react with hydroxylamines with ring opening to give 1,4-dioximes and the ring nitrogen is expelled as ammonia [82CC800] (scheme 4.1.2).



Scheme 4.1.2

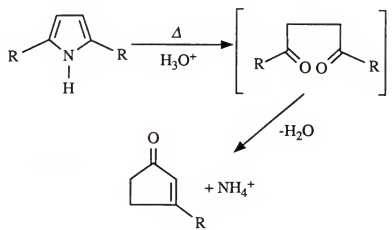
Pyridines also undergo ring opening reactions. Thus, 2,6-dimethylpyridine reacts with methyl iodide to form the 1-methylpyridinium cation (A) (scheme 4.1.3).



Scheme 4.1.3

Under alkaline hydrolysis conditions at 150°C, this cation undergoes ring opening to the intermediate (B) which then ring closes to give m-cresol and methylamine [85MI1] (scheme 4.1.3).

Whereas these methods are of little practical importance for a heteroatom removal, they offer useful hints. A more feasible approach would be the removal of heteroatoms with water as a solvent at high temperature and pressure in the presence of acid, as shown in scheme 4.1.4 below.



Scheme 4.1.4

It is envisioned that, under these conditions, the pyrrole ring cleaves to give the 1,4-diketone, which then would undergo ring closure, whereas the nitrogen becomes fixed as ammonium. To investigate this possibility, several pyrroles and indoles were chosen as model compounds. The reactions of pyrrole, 2,5-dimethylpyrrole, indole, 2-methylindole, 3-methylindole and 2,3-dimethylindole have been investigated in cyclohexane, in water and in 10% aqueous phosphoric acid. The standard conditions were 250°C for five days (see also Chapter 3); however, the reaction time and temperature was varied with the reactivity of the model compound. Table 4.2.1 will list

the GC behavior of all compounds encountered as starting materials and/or products. Table 4.2.2 shows the mass spectral fragmentation and properties of compounds used as starting materials and for the identification of products. Tables 4.2.3 and 4.2.4 record the mass spectral fragmentation patterns of all compounds for which authentic samples were not available and which were identified by comparison with published MS (Table 4.2.3) or by deduction of their structures from their MS fragmentation patterns (Table 4). The results obtained are presented in Tables 4.2.5 and 4.2.6. All quantities are given in mole% and are corrected with regard to their response factors (see Table 2.1, Chapter 2).

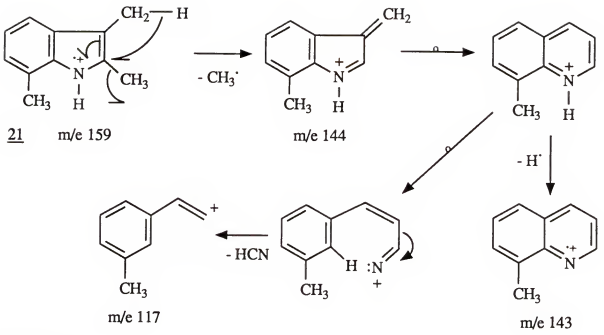
4.2 Pyrroles and Their Benzo Derivatives

4.2.1 Assignment of Stuctures

The structures of the products **(21)** and **(22)** were deduced from their mass spectra (Table 4.2.4).

2,3,7-Trimethylindole **(21)** shows a molecular ion peak at m/e 159 and a base peak at m/e 158 (M^+ - 1). Loss of a methyl radical from the M^+ peak leads to the fragment m/e 144, which rearranges to a 8-methylquinolinium cation. Loss of H· from fragment m/e 144 gives the corresponding radical cation at m/e 143 . Cleavage of HCN from the 8-methylquinolinium cation gives the fragment at m/e 117 [767MI1(j)] (scheme 4.2.1).

2,3,5,7-Tetramethylindole **(22)** displays a strong molecular ion peak at m/e 173 along with the base peak at m/e 172 (M^+ - 1). Similar to **(21)** loss of a methyl radical (CH_3·) leads to the fragment at m/e 158. After rearrangement to a 6,8-dimethylquinolinium cation loss of HCN occurs to give the fragment m/e 131. Loss of a hydrogen atom and a methyl radical gives the fragments m/e 130 and m/e 115.



21 m/e 159 m/e 144 m/e 117 m/e 143

Scheme 4.2.1

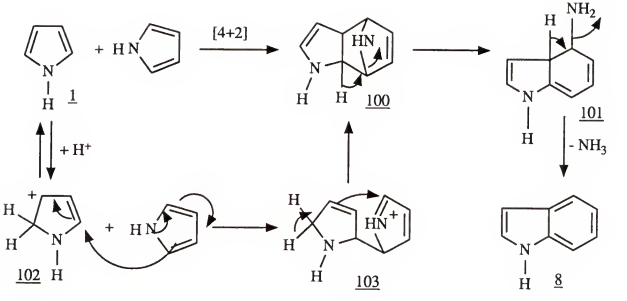
4.2.2 Discussion of Results

Pyrrole **(1)** (Table 4.2.5). Pyrrole decomposes at 850°C [77MI2] into hydrogen cyanide as the major decomposition product. Therefore, the low reactivity under thermal conditions at 250°C in cyclohexane is not surprising, and 99.5% of the starting material can be recovered. The same low reactivity is observed in water under equal conditions, where 99.2% of the starting material remains. The reaction products derive from

i) addition reaction (compound **8**), and

ii) polymerization.

Indole **(8)** is probably formed via a Diels - Alder or a cationic mechanism as shown in scheme 4.2.2. Pyrrole **(1)** adds to the protonated species **(102)**. The intermediate **(103)** ring closes under loss of a proton to the tricyclic structure **(100)**.



Scheme 4.2.2

Aromatization of **(101)** then leads to indole **(8)** via the extrusion of ammonia. However, the observation that indole is not found under thermal conditions suggests that the cycloaddition proceeds step-wise (ionic mechanism) rather than concertedly [77MI2]. Pyrrole is well known to undergo acid catalyzed polymerization [84MI2] and, therefore, the reactivity in acid is expected to be much higher. Thus, after 1.5 hours at 250°C with phosphoric acid as additive, pyrrole is completely consumed to give a brown, insoluble product, which presumably is a mixture of pyrrole oligomers.

2,5-Dimethylpyrrole **(3)** (Table 4.2.5). Under thermal conditions at 250°C in cyclohexane, no reaction is observed. Under the same conditions in water the conversion is 65%, whereas 2,5-dimethylpyrrole is completely consumed in aqueous phosphoric acid after 5 days at 250°C. The overall reaction pathways are

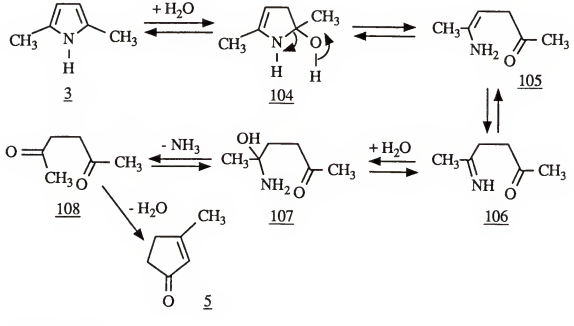
i) ring opening and loss of nitrogen (compound **5**),

ii) methyl transfer reactions (compounds **2, 4, 110** and **115**),

iii) cycloaddition reactions (products **12, 14, 15, 16** and **18**), and

iv) formation of oligomers and polymers.

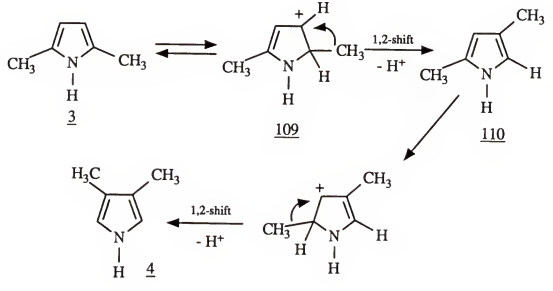
In water ring opening takes place and nitrogen is expelled as ammonia. The major product is 3-methylcyclopent-2-en-1-one (scheme 4.2.3). Addition of water to (**3**) gives the intermediate (**104**) which then ring opens to the enamine (**105**) which isomerizes to the more stable imine structure (**106**).



Scheme 4.2.3

Addition of water to the imine (**106**) and loss of ammonia from intermediate (**107**) results in the formation of the 1,4-diketone (**108**) which then undergoes condensation to the cyclic ketone (**5**). Minor products are 2-methylpyrrole (**2**), 3,4-dimethylpyrrole (**4**), and 2,4,7-trimethyl-2,3-dihydro-1H-inden-2-en-1-one (**15**).

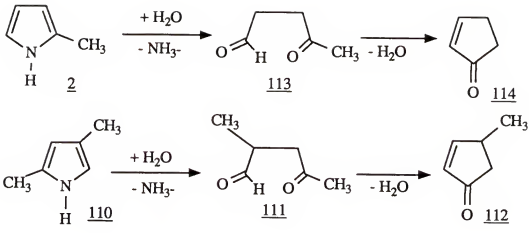
Presumably (**4**) is formed via the intermediate 3,5-dimethylpyrrole (**110**). Protonation of 2,5-dimethylpyrrole (**3**) at the 2-position furnishes the cation (**109**), which then undergoes a 1,2-methyl shift to give (**110**). In a similar way 3,4-d imethylpyrrole (**4**) is formed from (**110**) (scheme 4.2.4). This scrambling of methyl groups is also observed for the sulfur analog 2,5-dimethylthiophene [89EF6ip]. Under aqueous conditions 3-methylcyclopent-2-en-1-one (**5**) is the only ketone formed. With phosphoric acid as additive the additional ketones (**112**), (**114**) and (**115**) must have been intermediates to give the observed cycloaddition products (**12**), (**14**), (**15**), (**16**) and (**18**).



3 109 110 4

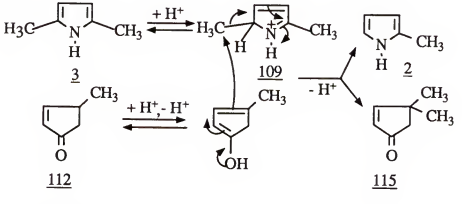
Scheme 4.2.4

Similar to the proposed mechanism in scheme 4.2.3., the ketones (**112**) and (**114**) are derived from the corresponding pyrroles (**2**) and (**110**) (scheme 4.2.5). However, ketone (**112**) may also have formed through double bond isomerization of (**5**).



Scheme 4.2.5

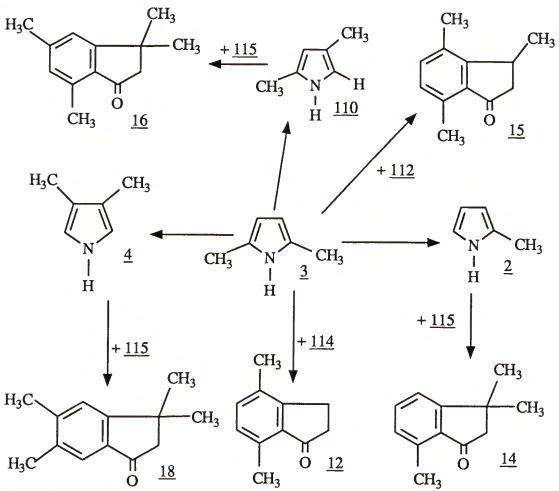
The presence of 4,4-dimethylcyclopent-2-en-1-one **(115)** and 2-methylpyrrole **(2)** is probably the result of a methyl transfer between the protonated 2,5-dimethylpyrrole **(109)** and 4-methylcyclopent-2-en-1-one **(112)** (scheme 4.2.6).



Scheme 4.2.6

In water alone at 250°C, ketone **(5)** was the major product with only a small amount (4.3%) of the cycloaddition product **(15)** present. Now, under acidic conditions, ketones **(112)**, **(114)** and **(115)** undergo cycloaddition reactions with pyrroles **(2)**, **(3)**, **(4)**

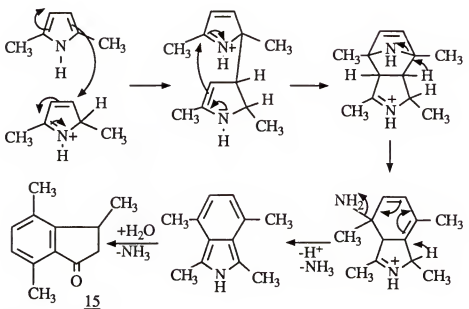
and **(110)** to form the products **(12), (14), (15), (16)** and **(18)** with loss of ammonia (scheme 4.2.7). Clearly, the reaction is acid catalyzed, which suggests that the cycloaddition proceeds step-wise via an ionic mechanism .



Scheme 4.2.7

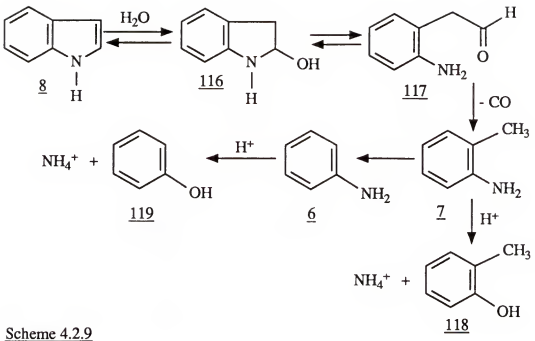
An alternative mechanism for the formation of **(15)**, for example, would be the self-addition of 2,5-dimethylpyrrole **(3)** leading to an isoindole structure, which then on hydrolysis forms compound **(15)**, as shown in scheme 4.2.8 [68JCS(C)3036].

In the same way the indenone derivative (**12**) can be obtained from 2,5-dimethylpyrrole (**3**) and 2-methylpyrrole (**2**).



Scheme 4.2.8

Indole (**8**) (Table 4.2.6). Indoles are much less reactive than pyrroles and the removal of nitrogen is more difficult due to the greater resistance of the carbon-nitrogen bond to hydrolysis. After 5 days at 250°C in water or cyclohexane, the starting material is completely recovered. For 5 days at 350°C indole reacts to only 1% in water or cyclohexane. Ring opening does occur in water at 350°C, but no heteroatom removal is observed (small amounts of 2-methylaniline (**7**) and aniline (**6**) are found). With acid catalysis indole is completely consumed after 2.5 days at 350°C, leaving an insoluble char. Methylene chloride washings of this char show mostly aniline (**6**) and o- and p-alkylanilines, together with some phenol (**119**) and o-cresol (**118**), indicating hetero-atom removal. The mechanistic pathway of their formation is shown in scheme 4.2.9.

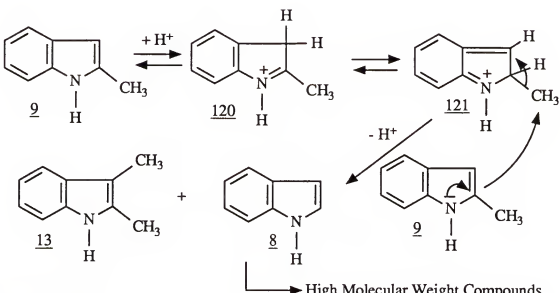


Scheme 4.2.9

Addition of water to indole **(8)** is followed by opening of the five membered ring to give the aldehyde **(117)** which loses CO to form o-methylaniline **(7)**. Demethylation of **(7)** [89EF7ip] and ipso substitution of the amino function with water give o-cresol **(118)** and phenol **(119)**.

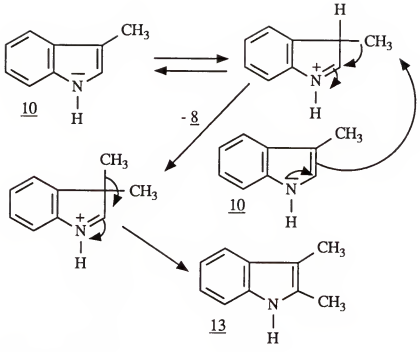
2-Methylindole **(9)** (Table 4.2.5). 2-Methylindole **(9)** is somewhat more reactive than indole **(8)**, but still no conversion is found under thermal or aqueous conditions at 250°C or 350°C for 5 days. With acid catalysis at 250°C, a 5% conversion takes place and the major product is 2,3-dimethylindole **(13)**, along with traces of indole **(8)** and o-methylaniline **(7)**. According to the proposed mechanism (scheme 4.2.10), one would expect equal amounts of 2,3-dimethylindole **(13)** and indole **(8)**. The GC-trace, however, shows only small amounts of indole **(8)**. A possible explanation may be the formation of high molecular weight compounds [70MI1], which were not eluted on the GC-column. A likely mechanism for the formation of **(13)** is shown below.

2-Methylindole **(9)** is protonated at the 3-position and is in equilibrium with structures **(120)** and **(121)** which act as methyl donors. Another molecule **(9)** then abstracts a methyl cation from **(121)** to form 2,3-dimethylindole **(13)** and indole **(9)** (scheme 4.2.10).



Scheme 4.2.10

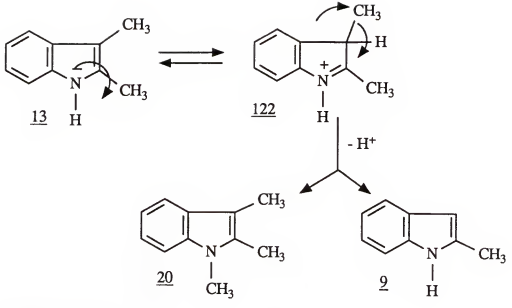
3-Methylindole **(10)** (Table 4.2.5). 3-Methylindole, as 2-methylindole, is unreactive at 250°C under thermal and aqueous conditions. In the presence of phosphoric acid the major product is 2,3-dimethylindole **(13)**, formed via an inter-molecular methyl transfer similar to the reaction pattern observed with 2-methylindole (scheme 4.2.11).



Scheme 4.2.11

Small amounts of indole **(8)** and 1,2,3-trimethylindole **(20)** are also present, but no 2-methylindole **(9)** has been found. Aniline **(6)** and o-cresol **(118)** are found in small amounts (see also scheme 4.2.9) [89EF7ip]. After 5 days at 350°C with acid as additive, the amount of o-cresol **(118)** and phenol **(119)** increases. Significant amounts of tar and polymeric products are also formed. Under these conditions no starting material was recovered.

2,3-Dimethylindole **(13)** (Table 4.2.5). The major products are 2-methylindole **(9)** and 1,2,3-trimethylindole **(20)** in water at 350°C and with acid as additive at 250°C for 5 days. The formation of **(9)** and **(20)** proceeds via a similar intermolecular methyl transfer as already shown for 2-methylindole **(9)**. 2,3-Dimethylindole **(13)** is protonated at the 3-position to form **(122)** which then reacts with a second molecule of unprotonated 2,3-dimethylindole to give **(9)** and **(20)** (scheme 4.2.12).



Scheme 4.2.12

No conversion is found under thermal or aqueous conditions at 250°C for 5 days, but no starting material was recovered after 5 days at 350°C in aqueous phosphoric acid. The reaction product is charred and largely insoluble. The methylene chloride extract showed mainly aniline (**6**), o-cresol (**118**) and phenol (**119**).

Table 4.2.1 Structure and Identification of Starting Materials and Products.

No.	RT min.	Structure	Mol. Wt.	Equiv. Wt.	Ident. Basis*	Response Factor
1	0.60	Pyrrole	67	67	T3	0.73
2	0.87	2-Methylpyrrole	81	81	T4	0.72
3	1.48	2,5-Dimethylpyrrole	95	95	T3	0.72
4	1.52	3,4-Dimethylpyrrole	95	95	T3	0.72
5	1.69	3-Methylcyclopent-2-en-1-one	96	96	T3	0.79
6	1.89	Aniline	93	93	T3	0.72
7	3.02	2-Methylaniline	107	107	T3	0.71
8	5.98	Indole	117	117	T3	0.71
9	7.14	2-Methylindole	131	131	T3	0.70
10	7.23	3-Methylindole	131	131	T3	0.70
11	8.15	5,7-Dimethylindole	145	145	T3	0.70
12	8.25	4,7-Dimethyl-2,3-dihydro -1H-inden-1-one	174	87	T3	0.70
13	8.46	2,3-Dimethylindole	145	145	T3	0.70
14	8.55	3,3,6-Trimethyl-2,3-dihydro -1H-inden-1-one	174	87	T3	0.76
15	8.62	3,4,7-Trimethyl-2,3-dihydro -1H-inden-1-one	174	87	T3	0.76
16	8.77	3,3,5,7-Tetramethyl-2,3-di-hydro-1H-inden-1-one	188	94	T3	0.76
17	9.34	2,3,5-Trimethylindole	159	159	T3	0.69
18	9.43	3,3,5,6-Tetramethyl-2,3-di-hydro-1H-inden-1-one	188	94	T3	0.76
19	9.45	5,6,7-Trimethylindole	159	159	T3	0.69
20	9.66	1,2,3-Trimethylindole	159	159	T3	0.69
21	10.14	2,3,7-Trimethylindole	159	159	T4	0.69
22	11.19	2,3,5,7-Tetramethylindole	173	173	T4	0.69

*T2= Table 4.2.2, T3= Table 4.2.3, T4= Table 4.2.4

Table 4.2.2 Properties of Authentic Compounds Used as Starting Materials and for the Identification of Products.

			Original		Purified			
No.	Compound	M.W.	Source[a]	Purity (%)	Method	Purity (%)	m/z (% rel. intensity) m/z (% rel. intensity) reported	Ref.[b] page
1	Pyrrole	67	K	94.0	dist.	99.0	67(100); 41(26); 40(6); 39(4); 38(2) 67(100); 41(58); 40(50); 39(62); 38(12)	12
3	2,5-Dimethylpyrrole	95	A	99.2	-	-	96(19); 95(94); 94(100); 80(22); 42 (19) 96(4); 95(58); 94(100); 80(17); 42(15)	61
8	Indole	117	A	99.5	-	-	118(8); 117(100); 116(7); 90(39); 89(41) 118(9); 117(100); 116(8); 90(33); 89(21)	177
9	2-Methylindole	131	A	99.9	-	-	131(66); 130(100); 77(15); 65;(6); 51(13) 131(79); 130(100); 77(15); 65(11); 51(11)	277
10	3-Methylindole	131	A	99.9	-	-	131(61); 130(100); 103(13); 77(22); 51(20) 131(88); 130(100); 103(9); 77(14); 51(8)	277
13	2,3-Dimethylindole	145	A	99.9	-	-	145(73); 144(100); 143(12); 130(59); 77(12) 145(80); 144(100); 143(13); 130(41); 77(12)	406

[a] A= Aldrich K= Kodak

[b] Heller,S.R.; Milne,G.W. EPA/NIH Mass Spectral Data Base, NBS, 1978-1980

Table 4.2.3 Identification of Products by Comparison of Mass Spectral Fragmentation with Literature Data.

No.	Compound	MW	Fragmentation Found m/z (% rel. intensity)	Ref. Page	Fragmentation Reported m/z (% rel. intensity)[b]
2	2-Methylpyrrole	81	81(72); 80(100); 53(35); 40(27); 39(18)	30	81(60); 80(100); 53(26); 40(3); 39(4)
4	3,4-Dimethylpyrrole	95	95(91); 94(100); 93(9); 80(29); 67(12)	61	95(96); 94(100); 93(13); 80(27); 67(12)
5	3-Methylcyclopent-2-en-1-one	96	96(84); 81(45); 67(100); 53(92); 39(37)	63	96(100); 81(37); 67(57); 53(54); 39(36)
6	Aniline	93	93(100); 92(9); 66(55); 65(73); 39(6)	58	93(100); 92(11); 66(33); 65(18); 39(18)
7	o-Methylaniline	106	107(67); 106(100); 79(18); 77(21); 39(4)	113	107(83); 106(100); 79(13); 77(17); 39(12)
11	5,7-Dimethylindole	145	145(68); 144(100); 130(27); 115(15); 51(11)	407	145(100); 144(73); 130(63); 115(12); 51(4)
12	4,7-Dimethyl-2,3-dihydro-1H-inden-1-one	160	160(62); 132(30); 131(19); 117(100); 115(53)	611	160(100); 132(23); 131(23); 117(73); 115(30)
14	3,3,6-Trimethyl-2,3-dihydro-1H-inden-1-one	174	174(45); 160(11); 159(100); 116(13); 115(40)	827	174(30); 160(12); 159(100); 116(11); 115(17)
15	3,4,7-Trimethyl-2,3-dihydro-1H-inden-1-one	174	174(36); 160(10); 159(100); 131(41); 115(17)	826	174(71); 160(12); 159(100); 131(21); 115(21)
16	3,3,5,7-Tetramethyl-2,3-dihydro-1H-inden-1-one	188	188(36); 174(12); 173(100); 128(28); 115(24)	1025	188(37); 174(13); 173(100); 128(11); 115(11)
17	2,3,5-Trimethylindole	159	159(78); 158(100); 157(6); 144(53); 115(12)	4215	159(88); 158(100); 157(9); 144(43); 115(10)
18	3,3,5,6-Tetramethyl-2,3-dihydro-1H-inden-1-one	188	188(36); 174(10); 173(100); 128(33); 115(30)	1026	188(29); 174(14); 173(100); 128(10); 115(11)
19	5,6,7-Trimethylindole	159	159(47); 158(80); 145(48); 144(100); 143(18)	594	159(92); 158(47); 145(15); 144(100); 143(12)
20	1,2,3-Trimethylindole	159	159(93); 158(100); 144(51); 143(11); 115(27)	594	159(87); 158(100); 144(57); 143(21); 115(18)

[b] Heller,S.R.; Milne,G.W. EPA/NIH Mass Spectral Data Base, NBS, 1978-1980

Table 4.2.4 Identification of Products from Mass Spectral Fragmentation Patterns.

No.	Compound	MW	Fragmentation Pattern [(% rel. intensity), structure of fragment ion]
21	2,3,7-Trimethylindole	159	159(75, M); 158(100, M-1); 144(75, M-15); 143(18, $C_{10}H_{10}N^+$); 115(23, $C_9H_7^+$)
22	2,3,5,7-Tetramethylindole	173	173(78, M); 172(100, M-1); 158(78, M-15); 143(33, $C_{10}H_{10}N^+$); 115(20, $C_9H_7^+$)

Table 4.2.5 Products [mole%] of 2-Methylindole **(2)**, Pyrrole **(1)** and 2,5-Dimethylpyrrole **(3)** Reactions.

	Compound	2-Methylindole					Pyrrole			2,5-Dimethylpyrrole		
	Solvent	H_2O	C_6H_{12}	H_2O	H_2O	C_6H_{12}	H_2O	C_6H_{12}	H_2O	H_2O	C_6H_{12}	H_2O
	Additive	-	-	H_3PO_4	-	-	-	-	H_3PO_4	-	-	H_3PO_4
	Temp (^oC)	250	250	250	350	350	250	250	250	250	250	250
	Time (days)	5	5	5	5	5	5	5	5	5	5	5
1	Pyrrole	-	-	-	-	-	99.2	99.5	-	-	-	-
2	2-Methylpyrrole	-	-	-	-	-	-	-	-	4.5	-	2.8
3	2,5-Dimethylpyrrole	-	-	-	-	-	-	-	-	35.4	100	-
4	3,4-Dimethylpyrrole	-	-	-	-	-	-	-	-	9.4	-	-
5	3-Methylcyclopentenone	-	-	-	-	-	-	-	-	46.4	-	-
8	Indole	-	-	-	-	-	0.8	-	-	-	-	-
9	2-Methylindole	100.0	100.0	94.8	100.0	100.0	-	-	-	-	-	-
12	4,7-Dimethyl-2,3-dihydro-1-H-inden-1-one	-	-	-	-	-	-	-	-	-	-	3.2
13	2,3-Dimethylindole	-	-	5.2	-	-	-	-	-	-	-	-
14	3,3,6-Trimethyl-2,3-dihydro-1H-inden-1-one	-	-	-	-	-	-	-	-	-	-	9.5
15	3,4,7-Trimethyl-2,3-dihydro-1H-inden-1-one	-	-	-	-	-	-	-	-	4.3	-	14.4
16	3,3,5,7-Tetramethyl-2,3-dihydro-1H-inden-1-one	-	-	-	-	-	-	-	-	-	-	21.0
18	3,3,4,5-Ttetramethyl-2-3-dihydro-1H-inden-1-one	-	-	-	-	-	-	-	-	-	-	8.2
	Unresolved peaks	0.0	0.0	0.0	0.0	0.0	-	0.5	100*	-	-	39.9

*Tar

Table 4.2.6 Products [mole%] of 3-Methylindole **(10)**, 2,3-Dimethylindole **(13)** and Indole **(8)** Reactions.

	Compound	3-Methylindole					2,3-Dimethylindole					Indole		
	Solvent	H_2O	C_6H_{12}	H_2O	H_2O	C_6H_{12}	H_2O	C_6H_{12}	H_2O	H_2O	C_6H_{12}	H_2O	H_2O	C_6H_{12}
	Additive	-	-	H_3PO_4	-	-	-	-	H_3PO_4	-	-	H_3PO_4	-	-
	Temp (^oC)	250	250	250	350	350	250	250	250	350	350	250	350	350
	Time (days)	5	5	5	5	5	5	5	5	5	5	5	5	5
No	Structure													
6	Aniline	-	-	1.2	-	-	-	-	-	-	-	-	0.8	-
7	o-Methylaniline	-	-	-	0.9	-	-	-	-	-	-	-	0.8	-
8	Indole	-	-	1.7	14.2	-	-	-	-	0.9	-	100.0	98.4	99.0
9	2-Methylindole	-	-	-	-	-	-	-	15.0	24.2	2.2	-	-	-
10	3-Methylindole	100.0	100.0	75.9	70.9	97.7	-	-	-	-	-	-	-	-
11	5,7-Dimethylindole	-	-	-	-	-	-	-	-	0.7	-	-	-	-
13	2,3-Dimethylindole	-	-	20.1	13.9	-	100.0	100.0	60.0	56.9	96.0	-	-	-
17	2,3,5-Trimethylindole	-	-	-	-	-	-	-	-	1.5	-	-	-	-
19	5,6,7-Trimethylindole	-	-	-	-	-	-	-	-	0.6	-	-	-	-
20	1,2,3-Trimethylindole	-	-	0.8	-	-	-	-	25.0	13.4	-	-	-	-
21	2,3,7-Trimethylindole	-	-	-	-	-	-	-	-	1.1	-	-	-	-
22	2,3,5,7-Tetramethylindole	-	-	-	-	-	-	-	-	0.2	-	-	-	-
	Unresolved peaks	-	-	0.3	0.1	2.3	0.0	0.0	0.0	0.5	1.8	-	-	1.0

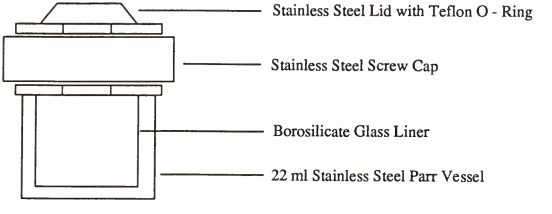
4.3 Conclusion

Pyrrole (**1**) is the most reactive compound in this series and rapidly undergoes polymerization at 250°C for 1.5 hours in the presence of acid. In cyclohexane for 5 days at 250°C, however, no reaction occured. Also, under aqueous conditions only a small amount of the cycloaddition product indole (**8**) was present. 2,5-Dimethylpyrrole (**3**), on the other hand, showed a conversion of 65% in water alone at 250°C for 5 days. The major product was the expected 3-methylcyclopent-2-en-1-one (**5**) which is evidence for a successful heteroatom removal. Indoles (**8**) - (**10**) and (**13**) were very stable under standard conditions. The major reaction pathways of the indoles (**9**), (**10**) and (**13**) was an intermolecular methyl transfers. In aqueous phosphoric acid, partial ring opening was observed at 250°C and 5 days. An increase in temperature to 350°C under aqueous conditions with added phosphoric acid leads to charring and tar formation, together with insoluble polymeric products. Methylene chloride extracts of the residues showed a breakdown of the indoles to aniline and alkylanilines, and o-cresol and phenol, indicating nitrogen removal from the aromatic ring.

CHAPTER 5
EXPERIMENTAL

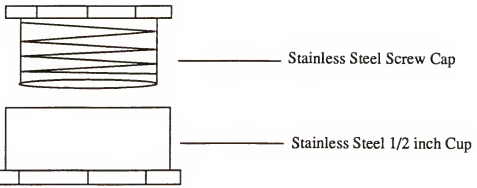
5.1 Procedure

All starting materials were analyzed by GC before use and purified if necessary until the impurity level was below 1%. One gram of compound (purity ≥ 99.0% by GC) and 7 ml of water, cyclohexane or 10% H_3PO_4 was placed in a 22 ml 303 stainless steel Parr screw cap vessel with a teflon o-ring gasket and a glass liner inside (borosilicate) (figure 5.1.1). Because of the thermal properties of teflon, the reactions at 350°C were carried out in a 10 ml stainless steel cup with a screw cap and no o-ring. The "cup-bombs" were self-sealing in a Swage-lock manner (figure 5.1.2). With the current reactor design, neither system was equipped for gas collection. However, a positive gas pressure was often observed while opening the reactors. The reaction vessel was purged with argon, sealed, and then heated in a fluidized sandbath.



Reactor for Temperatures up to 250°C

Figure 5.1.1



Reactor for Temperatures up to 350°C
Figure 5.1.2

The temperature was controlled with a digital thermo-control device to ± 5°C. Water was distilled and deionized, and was then deoxygenated by passing argon through. Cyclohexane was used as received from Aldrich, but argon was passed through for deoxygenation. After the reaction time was completed, the vessels were removed from the sandbath and left to equilibrate to room temperature (~ 2 hours).

The work-up procedure for the aqueous runs was essentially equal for all experiments. After completion of the reaction the aqueous mixture was transferred into a glass jar equipped with a teflon stirring bar. The glass liner, the inside of the bomb, and the cap were rinsed with a total volume of 10 ml of diethyl ether. This wash was then added to the aqueous mixture in the jar. After purging with nitrogen or argon the glass jar was sealed and the contents stirred over night at room temperature. The layers were separated and analyzed by GC and GC/MS. Solids which were left after stirring over night were centrifuged for approximately 30 min at 2000 rpm and analyzed by standard methods. For the cyclohexane runs 5 ml of cyclohexane were used to rinse the glass liner and the vessel. The cyclohexane mixtures could normally be injected directly into the GC or GC/MS. The procedure for the heterocyclic model compounds was the same

with regard to the runs in water and cyclohexane. Generally, acid runs were neutralized (pH 7) with sodium hydroxide solution before extraction with ether or methylene chloride. All analyses were carried out immediately after extraction.

5.2 Quantification and Identification

A Hewlett-Packard gas chromatograph Model HP 5890 equipped with a split injection port and a 15 m SPB-1 Supelco capillary column was used to determine the product distriubtion. To obtain comparable retention times the oven temperature was programmed to 50°C for 1 min, then increase 10°C/min up to 250°C, and held there for 10 min.

All conversions and yields are given in terms of moles as a percentage of moles of starting material. To achieve this, the area under the GC peaks was determined with an electronic integrator (Hewlett Packhard Model 3390A) and divided by its corresponding response factor. The obtained value for each peak was divided by its equivalent molecular weight (see for example table 3.2.1) and then normalized to give mole %. The response factors were calculated using equation 7 on page 15. Example: phenylacetic acid, $PhCH_2CO_2H$, $C_8H_8O_2$. The corresponding x-values (from table 2.3.1) are: $x_2= 122$; $x_3= 8$; $x_4= 8$; $x_5= 2$; $x_{12}= 1$; $x_{13}= 1$;

$$\Rightarrow RF= 0.991 - 0.000908x_2 + 0.00234x_3 + 0.00276x_4 - 0.112x_5 + 0.00481x_{12} - 0.323x_{13} = 0.38 \text{ (all other x-values are 0)}$$

The response factors for the following compounds were determined experimentally on a Hewlett-Packhard HP5890 gas chromatograph equipped with FID and split injection port: benzene, toluene, benzaldehyde, acetophenone, phenylethane-1,2-diol, benzoic acid, and stilbene (for details see 89TCMip). A capillary column (Supelco SPB-1, 15m long) was used, with the split ratio 30:1. The flow rate of the

helium carrier gas, hydrogen, and air at 22°C were 5, 30, and 400 ml/min, respectively. The injector temperature was 200°C. All injections were made using programmed oven temperatures: 35°C for 1 min, then increasing by 20°C/min up to 250°C. The volume of sample injected was 1 μl with concentrations of about 2 μg/μl. The individual components were identified from their electron ionization (EI) spectra using a GC-MS Finnigan MAT benchtop Ion Trap Detector. For those samples where chemical ionization was necessary, a quadrupole GC/MS instrument (Finnigan MAT 4500) was used. Products were identified by the MS. This was achieved at three levels of decreasing reliability:

i) By direct comparison of the MS fragmentation pattern with that of the authentic compound obtained under essentially the same MS operating conditions. The major features of the MS are reported, together with a literature reference to the MS of the compound (if available). ii) By comparison of the MS fragmentation pattern with that for the same compound in a data-base or other literature source. In such cases the sources of the reference spectrum is always given, and the major features of both the experimental and the reference spectra are recorded. iii) By interpretation of the MS fragmentation pattern. Where the authentic compound was not available, and the spectrum had not been reported elsewhere, identification had to be based on the MS fragmentation pattern. In such cases the basis on which the assignment was made is explained.

The conversions and yields found are reproducible to ±5% with a maximum error of ca. 10%. The reliability of the response factor calculation is ±9%. For high molecular weight compounds, a molecular weight of 500 g/mol and a response factor of 1 was assumed. The main objective of this dissertation therefore was not the determination of precise quantities but rather the identification of reaction products, to discover reaction pathways and to suggest reasonable mechanisms.

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The references are designated by a number-letter code of which the first two digits (or the first four digits for references before 1900) denote the year of publication, the next one to four letters the source (journal or patent) and the final digits the page or patent number. Less common journals and books are given the code 'MI' for miscellaneous, the first digit following 'MI' designated the order that reference occurs in the text, i.e., the '2' following 'MI' in 76MI2 means that is is the second miscellaneous reference for the year 1976. A list of codes (in alphabetical order) is given below followed by the journal which they represent.

A lower-case two-letter code for works which have been accepted for publication or are currently being prepared for submission (ip) is given after the journal code.

Where the name of a journal has changed, the original journal code is retained (e.g., 'Organic magnetic Resonance' changed to 'Magnetic Resonance in Chemistry' in 1986, but both are designated OMR).

CODE	FULL TITLE
AC	Analytical Chemistry.
ACA	Analytica Chimica Acta.
ACS(B)	Acta Chemica Scandinavia (B).
ADC	Annales de Chimie.

Ag	Angewandte Chemie.
AG(E)	Angewandte Chemie International Edition (English).
AJR	Aostra Journal of Research.
BCG	Bericht der deutschen Chemischen Gesellschaft.
CC	Chemical Communications.
CN	Chemical and Engineering News.
CT	Chemtech.
DRP	Deutsches Reichspatent.
EF	Energy and Fuels.
FC	Prep. American Chemical Society Div. of Fuel Chemistry.
FU	Fuel.
HCA	Helvetica Chimica Acta.
JA	Journal of the American Chemical Society.
JAT	Journal of Analytical Toxicology.
JCH	Journal of Chromatographic Sciences.
JCHR	Journal of Chromatography.
JCS(C)	Journal of the Chemical Society Sect. C.
JCS(J)	Journal of the Chemical Society of Japan.
JGC	Journal of Gas Chromatography.
JOC	Journal of Organic Chemistry.
MA	Die Makromolekulare Chemie.
MI	Miscellaneous.
OG	Organic Geochemistry.
PAC	Pure Applied Chemistry.
SE	Science.
T	Tetrahedron.

TCM	Tetrahedron Computer Methodology.
TL	Tetrahedron Letters.
USP	United States Patent.
ip	in press or in preparation.

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89EF7ip	A. R. Katritzky, F. J. Luxem and M. Siskin, Energy and Fuels, Part 8.

BIOGRAPHICAL SKETCH

Franz J. Luxem was born on April 25, 1958, in Cologne, West Germany. After completing "Realschule" in 1974, he became an apprentice with Bayer AG in Leverkusen, where he was trained as a chemistry laboratory technician. He then enrolled in a "Technische Fachoberschule" and graduated in 1978 with the "Fachabitur," the pre-requisite for university studies. After serving 15 months of compulsory drudgery in the "Bundesluftwaffe" (Federal Air Force), he began studying Chemistry in Wuppertal (a nice city as long as one does not look at it). There he passed the exams for the "Vordiplom" in 1982. He then transferred to the University of Bonn in the nation's capital village, where he not only was awarded the "Diplom" in chemistry, but also met his future wife, Leslie Shouse, an exchange student from the United States (and a rotten cook).

From January 1986 to the present, he has been a teaching and research assistant in the Organic Division of the Chemistry Department at the University of Florida. He avidly plays table tennis (UF men's champ 1986) and soccer (two broken fingers 1989). He is a member of the Gesellschaft Deutscher Chemiker, American Chemical Society and the Deutsche Lebensrettungsgesellschaft. Fortunately for his wife, he is also a much better cook.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Alan R. Katritzky
Kenan Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December 1989

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